

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

Apparatus for estimation of water by the xylene distillation method. E. L. WISE. *Chem. Ztg.* 47, 438 (1923).—The device described resembles a thistle funnel, the narrow stem of which is graduated, while the wider upper part, to which a reflux condenser is attached, is provided with a side-tube, which is bent downwards and connected with a boiling flask. The substance under test is heated in the boiling flask with about 50 cc. of xylene, and sufficient xylene is placed in the distn. attachment to fill it to the side-tube. Water and xylene are returned by the reflux condenser; the water collects in the graduated stem, while xylene overflows by the side-tube back into the flask. In doing so it is preheated by the vapor coming from the flask, so that the boiling of the liquid in the latter is uninterrupted. The complete removal of the water from the substance requires only 15–30 min.

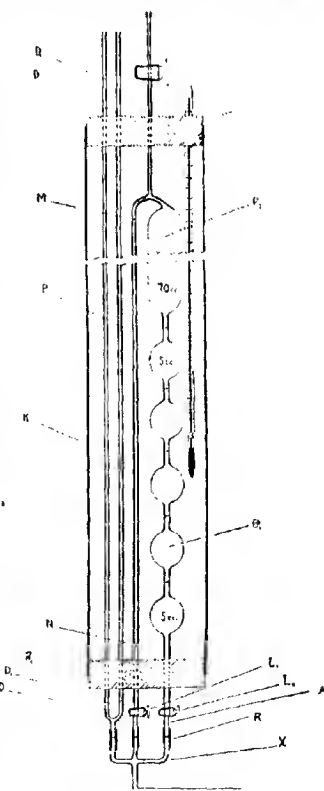
J. S. C. I.

Automatic apparatus for the estimation of water, especially in tar. R. MEZGER. *Gas u. Wasserfach* 66, 303–4 (1923).—One hundred g. of tar is heated with 50–75 cc. of xylene to the b. p. in a 300-cc. flask. The vapor passes through an insulated tube to a reflux condenser whence the condensed liquid flows to a 25-cc. graduated buret in which the water settles to the bottom while the excess xylene is returned to the flask through a side-tube at the top. The distn. is continued until the level of the water in the buret ceases to rise, when its vol. is read. The buret is then emptied and a new operation begun.

J. L. WILEY

Convenient form of buret for exact gas analysis. H. J. M. CREIGHTON. *Proc. Trans. Nova Scotian Inst. Sci.* 15, 115–7 (1919–20).—The buret, which is contained in a water-jacket, consists of a series of graduated bulbs, *B*, having a total vol. of 95 cc. and a tube, *M*, having a vol. of 5 cc. which is graduated in 0.01 cc. Two leveling tubes, *D*, connected with the buret as shown in the fig., are also enclosed in the water-jacket. Before the vol. of gas in the buret is read, the Hg is brought to the same level. H. J. C.

Apparatus for showing the isotherm of a gas. E. FAMIGLIANI. *N. R. cimento* 23, 393 (1922).—The app. consists of a



vertical iron tube to which several glass horizontal tubes are attached. The glass tubes are filled with the gas to be studied, while the iron tube is filled with Hg, which can be added as desired. By allowing varying quantities of Hg to enter the horizontal tubes, the gas is compressed, thus the meniscus in each tube forms a point on the isotherm. The app. must be carefully constructed to be successful. Precise specifications are given. A. W. C.

The beginning and the end of my work on the development of apparatus for crystal growth. L. WULFF. *Chem. App.* 10, 125-6 (1923).—Reminiscent. J. H. MOORE

A new colorimeter with absolutely symmetrical rays. K. BÜRGER. *Z. angew. Chem.* 36, 127-9 (1923); 3 cuts.—An immersion colorimeter, mounted on a stand like a microscope, the rays from the 2 tubes being thrown on the same field for comparison. Directions for operating are given. J. H. MOORE

Combustion analysis slide rule. ARTHUR GOHMANN. *Feuerungstechnik* 11, 49-51 (1922).—G. describes and illustrates a rather elaborate rule for the soln. of problems in combustion, such as the detn. of excess air, calcg. heat losses, and checking flue gas analyses. ERNEST W. THIELE

A new absorption and drying tower, a suitable heating oven for it, and their employment for the accurate drying of textile fibers. JULIUS OBERMILLER and MARTHA GOERTZ. *Z. angew. Chem.* 36, 429-32 (1923); 4 cuts.—The "tower" consists of a small glass cylindrical vessel of from 30 to 250 cc. capacity with outlet and inlet tubes on opposite sides near the top. A 2nd vessel of slightly smaller diam., with a hand-grip and neck for thermometer on top, slips into the vessel and fits with a ground joint at the top. At the inlet arm on the outer vessel the inner vessel bulges slightly inward freely to admit air or gas which passed down between the vessels to the bottom, then up through the inner vessel which contains the drying material, or material to be dried (wool, cotton, silk, etc.), then out through a small hole which registers with the exit arm on the outer vessel. The app. is made air-tight by turning the inner vessel a little. Directions for using are given. J. H. MOORE

New liquid manometers and their use in heating and ventilating practice. E. NICKEL. *Feuerungstechnik* 11, 137-40 (1923).—The form of draft gage described has a cylindrical well with axis horizontal, so that the gage can be used at different inclinations without affecting the zero reading. ERNEST W. THIELE

An improved stopcock. P. H. KOLLEWYN. *Ind. Eng. Chem.* 15, 1038 (1923). E. J. C.

Rubber lining for tube and ball mills. A. B. PARSONS. *Eng. Mining J.-Press* 116, 489-90 (1923).—More efficient. E. J. C.

Dehydrating oven. D. G. ZALOCOSTAS. *Can.* 234,302, Sept. 18, 1923.

Furnaces; gas producers, etc. J. J. DESCHAMPS. *Brit.* 192,069, Jan. 19, 1923. To facilitate phys. and chem. reactions in porous masses of material subjected to the action of fluids under pressure or undergoing distn., evapp. or chem. action, variations of pressure are produced in the chamber contg. the material under treatment by producing pulsations in the fluid or fluids supplied to or escaping from the chamber.

Evaporator for acids. CHEMISCHE FABRIK ZU SCHÖNINGEN UND DR. RICHARD VETTERLEIN. *Ger.* 307,564, Sept. 10, 1918. In evaporators for acids in which surface firing is employed in such a way that the hot gases moving in a direction contrary to that in which the acids flow pass into a reaction tower, the metal basin for the acids supports the tower and the acid pursues a zigzag course through the basin following a channel constructed of masonry. Peep holes and cleaning doofs are provided in the masonry walls.

Internal cooling of ozonizer. SIEMENS & HALSKE AKT.-GES. *Ger.* 314,722, Oct. 8, 1919. Between the surface of the cooling fluid in the inner pole and the junction place of the conductor for the cooling medium there is placed an insulation to prevent sparking.

Ozonizer. SIEMENS & HALSKE AKT.-GES. *Ger.* 312,642, June 3, 1919. The producer is in U-form and both legs of the U are used as ozonization tubes.

Briquetting coal, stone, etc. H. G. LLOYD and G. ST. BARBE. *Brit.* 195,414, Oct. 5, 1921. App. for mfg. coal, stone, etc., briquets with the aid of a binding agent comprises means for simultaneously feeding continuous streams of heated binding agent such as bitumen, pitch, etc., from a tank and water or wet steam from perforated pipes to a receptacle in which they intermingle and froth, and means for continuously delivering said froth from the receptacle through a conduit into contact with a stream of the material to be briquetted falling from a hopper. •

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

Frank Austin Gooch. P. E. BROWNING. *Ind. Eng. Chem.* **15**, 1088 9(1923).—A brief biography, with portrait. E. J. C.

Hans Goldschmidt. F. HABER. *Ber.* **56**, 77 9A(1923).—An obituary, with portrait. E. J. C.

The Fourth International Congress of Chemistry. JEAN GÉRARD. *Ind. Eng. Chem.* **15**, 1082-5(1923).—An abstract of the minutes of the Cambridge meeting, held June 17-20, 1923. Committee reports are given on nomenclature, bibliography, physicochem. standards, pure products for research, bibliography of industrial and technological products, choice of a thermochem. standard, tables of costs, ceramic products, food preservation, scientific and industrial ownership, and industrial hygiene. E. J. C.

Chemistry at the National Research Council. C. J. WEST. *Chem. Bull.* (Chicago) **10**, 207-11(1923). E. J. C.

The atomic weight of antimony from different sources. I. Preliminary. S. D. MUZAFFAR. *J. Am. Chem. Soc.* **45**, 2000-13(1923).—Metallic Sb was prepd. from stibinites from Hungary, Borneo, Peru, and Bolivia, and compared with KBiO_3 by soln. in H_2SO_4 , addn. of solid KBrO_3 and completion of the titration with 0.01 N KBrO_3 soln. The at. wts. of Sb were, for the resp. samples, 121.14, 121.56, 121.72, and 122.37. R. S. MULLIKEN

Modern methods of formulating the periodic system of the elements. FRITZ PANETH. *Z. anorg. Chem.* **36**, 307-30(1923).—A discussion accompanied by 3 tables designed: (1) to show the relation to at. structure especially according to Bohr, (2) for those who prefer the 'long period' form, and (3) for texts and references to take the place of the form ordinarily used. The form here presented differs from the ordinary one in placing the rare earths together in group III, and in showing the noble gases as transition elements related in some measure to the metals of group VIII. A. E. STRAIN

Simple method for determining apparent densities. K. C. DODDS. *Chem. Met. Eng.* **29**, 324-5(1923).—The apparent ds. of porous substances may be detd. as accurately by simple water displacement as by boiling first under reduced pressure. P. D. V. MANNING

The quadrivalence theory of Adolf Meyer. ANON. *Chem. Ztg.* **47**, 645 6(1923).—If the mols. of a gas move about freely in space it is necessary to assume a mutual attraction and repulsion between them in order that stable equl. may be explained, and this condition must obtain also in the atoms from which the mols. are made up. Spheres touching one another at 4 points (the corners of inscribed tetrahedra) would satisfy this condition, so it may be assumed that atoms really behave like spheres, and have valences or bonds at the 4 points indicated, to which atoms of the same or different kinds can be attached. Conclusions drawn from such a theory are illustrated by drawings and models, and the fundamental proposition is expressed thus: (a) Elements are classified into groups and series according to their electronegative and electropositive character, valence and at. wt.; (b) atoms of all elements are originally univalent; (c) these 4 valences are satd. by at. or mol. linkages whose sum is always 4; (d) these bonds can pass over from one kind to the other in accordance with conditions of temp. and state of matter concerned; and (e) every atom is bound to another by a single valence only. Meyer's theory has been applied with particular success to C and N compds. W. C. EBAUGH

Internal pressure and sphere of molecular action. W. HERZ. *Z. Elektrochem.* **29**, 338-9(1923).—The radius of the sphere of mol. action is twice as great as the mol. diameter. In homologous series of org. compds., the radii of the sphere of mol. action usually increase with mol. wt. Isomeric compds. have dissimilar spheres of action. H. JERMAIN CREIGHTON

Physical chemistry of the crystalline state. F. KÖRBER. *Z. Elektrochem.* **29**, 295-301(1923).—An address on X-ray analysis and the study of solids. H. J. C.

The crystal structure of potassium hydrogen fluoride. R. M. BOZORTH. *J. Am. Chem. Soc.* **45**, 2128-35(1923).—By taking the data from spectrum and Laue photographs and making some use of the results of the theory of space groups, it is shown that the following arrangement is possible for the tetragonal KHF_2 . The unit prism, which is 5.67 Å. on a side and 6.81 Å. high, contains 4 chem. mols. The coordinate positions of the constituent atoms are stated to be: F: $u, u + 1/2, 0; \bar{u}, 1/2 - u, 0; 1/2 - u, u, 0; u + 1/2, \bar{u}, 0; u + 1/2, u, 1/2; 1/2 - u, \bar{u}, 1/2; u, 1/2 - u, 1/2; \bar{u}, u + 1/2, 1/2$, where $u =$

0.14 \pm 0.01. K: $00\frac{1}{2}/4$; $00\frac{3}{4}/4$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}/4$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}/4$. H: apparently either $0\frac{1}{2}/0$; $\frac{1}{2}/0$; $\frac{1}{2}/\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}/4$, or $0\frac{1}{2}\frac{1}{2}/4$; $0\frac{1}{2}\frac{1}{2}\frac{1}{2}/4$; $\frac{1}{2}0\frac{1}{2}/4$; $\frac{1}{2}0\frac{1}{2}/4$.

RALPH W. G. WYCKOFF

The crystal structures of the cubic forms of arsenious and antimonious oxides. R. M. BOZORTH. *J. Am. Chem. Soc.* **45**, 1621-7(1923).—The crystal structures of the cubic modifications of As_2O_3 and Sb_2O_3 have been detd. by using data from spectrum and Laue photographs and applying the results of the theory of space groups. The unit cells each contg. 8 mols. of As_2O_3 or Sb_2O_3 have the lengths of edge of 11.06 Å. and 11.14 Å., resp. The O atoms have the arrangement 48c and the other atoms the arrangement 32b (Wyckoff, *Carnegie Institution Publication No. 318*). Values assigned to the parameters in these arrangements are the following: As, 0.895; Sb, 0.885; O in As_2O_3 , 0.21; O in Sb_2O_3 , 0.23. The resulting structure may be considered as a diamond arrangement of R_2O_4 mols.

RALPH W. G. WYCKOFF

The recrystallization of metals and salts. G. TAMMANN and Q. A. MANSURI. *Z. anorg.-allgem. Chem.* **126**, 119-28(1923).—Finely powd. material was heated with slow displacement by a special mech. stirring device. If this stirring is not too strong the temp. at which the mech. stirrer remains stationary represents the actual beginning of recrystn., and depends upon the vol. of the metallic powder, the mesh size, the stirring force, and the rate of heating. Fifteen cc. of metallic powder were heated in a 2-cm. glass tube at a rate of 10° per min. with a stirring force of 75 g. and 46 r. p. m. A H_2 atm. was used to prevent oxidation. Ag, Sn, Sh, Cu, Fe, Zn, Pb, Cd, Co and Al gave results varying from 120° to 150° . The recrystn. temp. has no relation to the m. p. of the metal. The temps. found in this study corresponded very closely to the temps. of the beginning of decrease in elec. resistance. Thirteen common salts under similar conditions showed the temp. of recrystn. to be directly proportional to the m. p. (40° for NH_4NO_3 and 316° for $PbSO_4$). The phenomena were more apparent with salts than with metallic powders.

W. A. MUDGE

The hundredth anniversary of the disputed question of isomorphism. J. I. SALAVSKII. *Ber. Polytchn. Ivanovo-Wosniessensk* **4**, 18-45; *Chem. Zentr.* **1922**, 111, 326-7.—An historical survey of the different opinions about isomorphism based on S.'s work (cf. *Ber. Polytchn. Ivanovo-Wosniessensk* 1 and 3) and in connection with the work of Gossner (*C. A.* **3**, 38) S. concludes, like Kopp and Dumas, that a close relation exists between mol. vol. and isomorphism. This is illustrated by complete tables of isomorphic compds. Possible objections to the views of Gossner are due to the fact that he chose the arithmetical instead of the geometrical relation in his comparison of mol. vols. Through comparison of data on various compds. a periodic regularity between mol. vol. and crystallographic consts. is established, viz., that like crystallographic forms correspond to like mol. vols. or stand in the relation of whole nos. to one another.

C. C. DAVIS

Atomic arrangement of magnetic and nonmagnetic nickel. F. WEVER. *Mitt. Kaiser Wilhelm-Inst. Eisenforsch.* **3**, 17-22(1922).—Hull's observation that Ni at ordinary temps. consists of two cryst. modifications, with different space lattices, could not be confirmed. Ni, both at ordinary temps., and between 400° and 650° , i. e., above the magnetic transformation point, has the same at. structure consisting of a face-centered cu. lattice with a parameter of 3.51×10^{-8} cm. The magnetic transformation of Ni is therefore of the same nature as that of iron and is not due to any allotropic change.

J. S. C. I.

The permeability of nickel to hydrogen. VICTOR LOMBARD. *Compt. rend.* **177**, 116-9(1923).—Expts. were conducted with disks of Ni to det. d , the vol. of H_2 in cc. at 0 and 760 mm., which penetrated one sq. cm. of Ni in one hr. The disks were 9.7 mm. in diam. and 0.3 and 0.4 mm. thick. In the case of the former with an approx. const. pressure of 775 mm. d varied from 27.8×10^{-2} cc. at 458° to 178×10^{-2} cc. at 598° , while for a disk 0.4 mm. thick it ranged from 4.83×10^{-2} cc. at 370° to 195×10^{-2} cc. at 693° . The results in both cases when plotted give curves of the form $d = at$, where t is the temp. and a is a const. At varying pressures for a disk 0.3 mm. thick and an approx. const. temp. of 590° d ranged from 152×10^{-2} cc. at 775 mm. to 14.6×10^{-2} cc. at 11 mm., and for the 0.4 mm. disk it varied from 77×10^{-2} cc. at 773 mm. to 16.8×10^{-2} cc. at 25.5 mm., the results giving a curve of the form $d = K\sqrt{P}$, where P is the pressure and K is a const. Values of a and K cannot be properly assigned to Ni, as they vary with the origin and previous treatment of the sample of metal.

R. G. FRANKLIN

Specific gravity of absolute ethyl alcohol at 20° . C. N. RIEBER. *Z. Elektrochem.* **29**, 334-8(1923).—Two l. EtOH (99.90%) were boiled with a soln. of Ca ethylate for 20 hrs., 100 cc. being allowed to distil over slowly. This distillate contained all of the aldehyde. During the period of heating a slow current of dry, purified H_2 was passed through the app. The alc. was then fractionated (3 fractions) and the middle fraction

(1600 cc.) used for the d. measurements. The value obtained for the d. of abs. EtOH, satd. with air, is $d_4^{20} = 0.789334 \pm 0.000003$. The value found by the Bureau of Standards is $d_4^{20} = 0.78934 \pm 0.00001$.

H. JERMAIN CREIGHTON

Dilatometric researches on potassium aluminum sulfate. (MILLER) E. N. IVANOVA. *J. Russ. Phys. Chem. Soc.* 48, 1905-16(1916).—It was noticed by Wiedeman (*Ann. Phys. Chem.* 17, 561-76) that K. alum contracts when heated above 51.3° in a dilatometer, and he explains this as being due to dissociation of the constituent mols. of the alum. This expt. was repeated, but no contraction was observed up to 87.3° , with either Hg or paraffin as the dilatometer liquid. The contraction observed by Wiedeman was probably due to the slow filling up of the interstices of the powd. alum by Hg. The use of paraffin above 75° is not recommended, as expansion of air adsorbed on the solid causes an abnormal expansion in the dilatometer. This adsorbed air is very difficult to eliminate.

Starch iodide. W. HALLGREN. *Svensk Farm. Tids.* 27, 357-65(1923).—An iodine powder of excellent keeping properties is prepd. by combining I with starch mechanically in the following way: The starch is heated 1 hr. at 60° then at $100-110^\circ$ to const. wt. One hundred parts of this starch are shaken in an Et₂O soln. of 5 parts l. The Et₂O is allowed to evaporate gradually. The powder is kept in colored glass bottles which are tightly stoppered. The color is brick red when wet with Et₂O, and grayish yellow when dry. When freshly prepd. the I content was 4.9%. At the end of 14 months it had dropped to 4.3%. The usual starch-iodide (blue) with a 5% I content dropped to 2.8% in the course of 8 days. No I crystals can be detected with the compound microscope. The prepn. becomes blue when moistened. The I can be almost completely removed by extg. with Et₂O or a similar I solvent. To distinguish the prepn. from the blue starch iodide H. prefers the Latin term Amylum cum Iodo (Ph.D.) in contrast to Iodurum Amyli (Ph.Belg.). The former term suggests a mixt., and the latter a compd.

A. R. ROSE

Properties of ideal gases. I. The molecular volumes of gases. P. N. PAVLOV. *J. Russ. Phys. Chem. Soc.* 49, 322-4(1917).—P. derives mathematically that $(p/T)_{\text{const.}} = K(1)$. That is, for ideal gases compared under corresponding conditions the pressure is proportional to the abs. temp. Further, $v_{\text{corr.}} = K(2)$, i. e., for ideal gases at corresponding conditions the mol. vol. is independent of the chem. nature of the substance. Equations (1) and (2) can be tested exptl. if the values of p/T and v at corresponding temps. and pressures are known. Previous papers have shown that $T_c = 1.6167 M\sqrt{n}$ and $P_c = 0.13076 M\sqrt{n}$, in which M = mol. wt. and n = no. of atoms in the mol. By the aid of these equations the values of $T_{\text{corr.}}$ and $p_{\text{corr.}}$ for N₂, H₂, NO, O₂, HCl, CO₂ are tabulated. From this calcn. it is found that the ratio $(p/T)_{\text{corr.}} = K = 0.003663$.

GEORGE W. PUCHER

The equation of state for pure nitrogen, gas phase. L. B. SMITH AND R. S. TAYLOR. *J. Am. Chem. Soc.* 45, 2107-24(1923).—The p, v, T relationships of pure gaseous N₂ were studied by the isometric method over the range of temp. from 0 to 200° and 30 to 330 atm. pressure. Within the limits of exptl. error the data are represented by the Keyes equation, $p_{\text{atm.}} = [2.92855 T/(v - \delta)] - [1623.63/(v + 0.2954)^2]$, where $\log \delta = 0.18683 - (0.3113/v)$. The wt. of a l. of N₂ at normal temp. and pressure was calcd. from the equation of state to be 1.2509 g. as compared with the generally accepted value of 1.2507 g. The compressibility coeff. at 0° was calcd. and found to be 0.00061 as compared with 0.00056 from Holborn and Otto's equation and the work of Rayleigh, and 0.00043 and 0.00044 from Chappuis and Maverick, resp.

F. L. BROWNE

Composition of oxygen and nitrogen mixtures as vapors and liquids between -183° and -193° . R. MEWES. *Z. Sauerstoff-Ind.* 14, 108(1922); *Chimie et industrie* 10, 73(1923).—If r and r' are the ratios of O to N in the liquid and gaseous phases which are in equil. between -183° and -193° (ratios which are given in Baly's tables), the ratio at one temp. can be found from that at a temp. 2° lower by multiplying the latter by 2. This rule is only approx. and can be approx. deduced from Baly's original formula: $\log r' = a + b \log r$.

A. PARINEAU-COUTURE

The transition in case of mechanical subdivision of crystalline hydrates of the water of hydration into adsorbed water. T. HAGIWARA. *Kolloid Z.* 32, 154-6(1923).—Al₂O₃·3H₂O and quartz dried to const. weight were ground in a *colloid mill* and then kept at higher temps. in the desiccator. Weighing showed that at a sufficiently fine state of subdivision of Al₂O₃·3H₂O its water of hydration loosens its firm bond and assumes the properties of adsorbed water.

A. MUTSCHELLER

A case of simultaneous positive and negative adsorption. M. A. RAKUZIN AND (MILLER) G. F. PEKARSKA. *J. Russ. Phys. Chem. Soc.* 48, 1889-90(1916).—The adsorption of Bismarck-brown by gelatin and by leather powder consists of both positive

and negative adsorption. The increase in the concn. of the soln. owing to adsorption of water, shows the latter, while the former is shown by the decolorization of the soln. An increase in the optical rotation of the soln. from 0 to $+0.55^\circ$ in the case of gelatin shows that some of the latter passes into soln. J. C. S.

Adsorption studies. I. Ion adsorption by freshly precipitated and air-dried manganese dioxide. N. G. CHATTERJI AND N. R. DHAR. *Kolloid-Z.* 33, 18-29 (1923).—The greater part of this work has already been reported by Chatterji, (see C. A. 17, 2214). Monovalent cations such as Ag^+ are adsorbed more completely than bivalent ones such as Cu^{++} , Ba^{++} , etc., and these in turn more completely than trivalent ions as Fe^{+++} and Al^{+++} . This confirms the Schulze-Hardy rule: "Our expts. show clearly that coagulating power and adsorption go hand in hand." F. L. BROWNE

The behavior of pumice stone during the dehydration of organic liquids. ARMIN. SEIDENBERG. *J. Assoc. Official Agr. Chem.* 7, 98-106 (1923).—Pumice stone, or any substance consisting of small particles or having numerous fine capillary openings, has a greatly increased tendency to adsorb liquids and gases, particularly after being heated. The wt. of material in this condition is affected to a marked degree by changes in temp. and pressure. It gains wt. after being heated while in a desiccator, and also during the process of weighing. For this reason also it readily adsorbs moisture from the atm. or from liquids spread over it. This adsorbed moisture is held very tenaciously and can only be removed by heating the pumice to redness. It appears that the presence of this adsorbed moisture has a decisive effect in accelerating the decompn. of org. residues distributed over the pumice. When the pumice is heated to redness before being used and all the moisture thus expelled, an approx. const. wt. may at times be obtained due to the balancing effect of 2 opposing errors. This const. wt. may or may not be correct and checks can usually be secured only by prepg. all the pumice used under identical conditions. Where the pumice is dehydrated at the comparatively low temps. used for the evapn. of the liquid it is not possible to secure significant results that will indicate the true amt. of solid matter present. If too low a temp. is used not all the H_2O is expelled, particularly in the presence of viscous material. With higher temps. it is not possible to secure a distinct end point that will clearly distinguish between the loss due to the decompn. of the solid and that due to the evapn. of the liquid portion, and it is not possible to attain a significant "const. wt." that indicates the correct result.

J. A. KENNEDY
The Gibbs theorem of surface tension applied to solutions of sodium abietate. RUDOLF LORENZ. *Kolloid-Z.* 33, 15-8 (1923).—There exists a close parallelism between the surface concn. of a freshly dil. soln. of Na abietate calcd. from the Gibbs principle and the measured surface tension of the soln. 5 hrs. after diln. F. L. B.

The structure of thin films. IV. Benzene derivatives. A condition of stability in monomolecular films. N. K. ANAM. *Proc. Roy. Soc. (London)* 103A, 676-87 (1923); cf. C. A. 16, 4107.—Derivs. of benzene such as hexadecyl phenol, contg. one long chain and one polar group in the β -position, orient on H_2O surfaces like fatty acids, the phenol group forming the head of the mol. in contact with the H_2O . Measurements of the cross-section of the head (C. A. 16, 4107) gave a result in good agreement with the corresponding cross-section of the nuclei of aromatic compds., deduced from Bragg's measurements on crystals. The relation between the films on H_2O and the mono-mol. layer which would be obtained by repeated cleavage of the crystal is explained. Films of these compds. show the usual phenomena of expansion to a two-dimensional vapor described in (C. A. 16, 4107). Compds. such as cetyl palmitate, palmitic anilide, etc., which contain one polar group placed between two chains, or one chain and a ring, do not adhere to a H_2O surface well enough to give measurable condensed films, though in the expanded state such films are often more stable. The β -sulfonic acids of hexadecyl and octadecyl benzene give soap-like solns. in H_2O . V. *Ibid* 687-95.—Br in the α -position, in the bromo acids and esters, increases the cross-section of the mols. in the films. The heads of bromo acids may pack in several different arrangements having areas from 32.8 Å.U. to 26 Å.U. The Br atom increases the soly. of films of the higher fatty acids. It also lowers the temp. of change from condensed to expanded films, but it does not appreciably affect the properties of the films, when expanded. The double linkage in the α,β -position relative to the $-\text{COOC}_2\text{H}_5$ group increases the cross-section of the mol. in the films, as it does in iso-oleic acid. The transition between two forms of condensed film, such as those found with the substituted ureas, seems exactly analogous to that between two polymorphs or allotropic modifications of solid substances. The law found in C. A. 16, 4107, giving the increase of the temp. of expansion of the films with increasing length of the hydrocarbon chains, has been confirmed on 8 homologous series. F. L. BROWNE

Quantitative studies on dispersoid systems according to the P. P. von Weimarn mechanical method. S. UZINO. *Kolloid-Z.* 32, 149-54 (1923).—A preliminary report that Se, Te, S, $\text{Al}(\text{OH})_3$, BaSO_4 , Sb_2S_3 , Ag, Hg, and Au ground in the *colloid mill* with grape sugar show a max. of stability not at finest subdivision. The greatest stability was observed to be 8 months.

The nature of electrical colloidal synthesis. SVEN BONFORS. *Svensk Kém. Tids.* 35, 136-40; *Kolloid-Z.* 33, 83-95 (1923).—A discussion of colloidal synthesis by sym.a.c. (cf. *C. A.* 17, 1362). The following is derived by mathematical formulation; $w = Rf = \sqrt{L/C}$. That is, the dispersed metal increases with the increase in self induction and decreases with the increase in capacity. Calcn. and observation are in good agreement. The agreement is far better if the cube root be substituted for the square root in the formula. This is merely an empirical substitution but must somehow represent a new property of the elec. cycle. The change in spark resistance is not quantitatively the same in these expts. on colloidal synthesis as for sparks in an air medium. This should be demonstrable by calorimetric measurements. B. is of the opinion that elec. colloidal synthesis is a thermal effect and not mech. (cf. Ostwald, *Kolloid Z.* 7, 132).

The dielectric constant of colloidal solutions. J. ERRERA. *Kolloid-Z.* 32, 157-63 (1923); cf. *C. A.* 16, 4123; 17, 908.—The dielec. const. of colloidal solns. is generally not much different from that of the pure solvent except in the case of V_2O_5 . The frequency of the current, its intensity and the temp. have a great decreasing influence upon the dielec. const. At wave length 295 m. it is 88.9; at 405 m., 103.9; and at 525 m., 114. During the running of a.c. the dielec. const. increases. The observed high dielec. const. of V_2O_5 seems not to be due to an actually higher cond. factor.

Protective colloids. X. Saponin as a protective colloid. 3. Colloidal selenium. A. GUTBIER AND U. RHEIN. *Kolloid-Z.* 33, 35-6 (1923); cf. *C. A.* 15, 3778. Saponin is a satisfactory protective colloid for colloidal Se produced by the reduction of SeO_2 by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The compn. and amt. of soln. used for the prepn. of Se colloids conlg. 0.008-0.07% Se (after dialysis) are discussed; e. g., a 0.02% Se colloid was produced from 50 parts of a 1:100 SeO_2 soln., 20 parts of a 1:100 saponin soln., and 10 parts of 1:500 N_2H_4 soln. The viscosity at 30° increases slowly with the age of the colloid. Reversible solid Se colloids could not be made by drying the above Se colloids over H_2SO_4 in a vacuum, nor by coagulation with alc. By careful evapn. of the Se colloid, mostly on the water bath at 40-50°, completely reversible solid colloids conlg. 33-13% Se were obtained.

Protective colloids. XIII. Ceratoniae siliquae glue as protective colloid. I. General colloido-chemical investigation of the glue of St. John's bread. H. LOCHER, K. KREIDL AND A. GUTBIER. *Kolloid-Z.* 33, 37-9 (1923).—The glue ext. of the Carob bean is prepd. by grinding the kernel, washing with cold water, and extg. for 2 to 3 days at 50-60° with water satd. with CHCl_3 . The clear yellow viscous liquid is filtered through cellulose or linen. The water soln. decomposes readily at room temp.; CHCl_3 has a stabilizing effect. By dialysis the ash content may be reduced to around 5%, without coagulation. To keep the glue stable, it is essential that it be kept cold, that light be excluded and that excess CHCl_3 be present. Otherwise a gelatinous ppt. forms and the soln. decreases in viscosity. The gluc solns. have a significant reducing action on Fehling soln. They increase in viscosity with increase in concn. They may be warmed to 90° and cooled without decompn. Electrolytes have slight effect on the viscosity.

Forces of adhesion in solution. II. Coagulation of coarse suspensions. SERGIUS WOSNESSENSKY. *Kolloid-Z.* 33, 32-4 (1923); cf. *C. A.* 17, 1572.—The coagulation by common electrolytes of coarse suspensions of kaolin, $\text{Al}(\text{OH})_3$, and Sb_2O_3 was studied. No single electrolytes, with the exceptions of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$, had any coagulating effect. Marked coagulation occurs with the simultaneous action of bivalent or trivalent metal salts and caustic alkalis, e. g., BaCl_2 and NaOH , or AlCl_3 and NaOH . These materials form difficultly sol. hydroxides, which are adsorbed on the surface of the particles of the suspension and cause coagulation by changing the forces of adhesion and cohesion. Materials such as NH_4Cl and tartaric acid which hinder the formation of hydroxides disturb the coagulation. The thickness of the adsorbed hydroxide is estd. to be of mol. dimensions.

Experimental studies of the coagulating powers of electrolyte series. AGNES IVANITZKA AND L. ORLOVA. *Kolloidchem. Beihfte* 18, 1-38 (1923).—The coagulating powers of several series of electrolytes were studied with the following hydrosols: negative—mastic, sulfosols of As_2S_3 and Sb_2S_3 , S, Au, Pt, Berlin blue, MnO_2 and $\text{Fe}(\text{OH})_3$; positive— Fe_2O_3 , Al_2O_3 , Cr_2O_3 and AgBr . In general, the anion series with a const.

cation is antivalent for negative sols and convalent for positive sols, whereas the cation series with a constant anion is convalent for negative sols and antivalent for positive sols. Comparative studies of electronegative suspensions of coal in alkaline media and electropositive suspensions of Fe_2O_3 in acid media were made with true sols and no marked differences were observed in their ability to coagulate by electrolytes. The following substances were added to the dispersion medium of the suspensions to determine their effect on their coagulation by electrolytes: MeOH , AcH , glycerol, Na protalbinat, dextrin and gelatin. Nonelectrolytes affect the stability of the suspensions as well as the rearrangement of the electrolytes series in their coagulating powers. Coagulation is considered to be not simply the result of physical factors, *i. e.*, surface tension, dielec. const., etc., but of relations among all components of the coagulating system, *i. e.*, disperse phase, dispersion medium and electrolytes. I. NEWTON KUGELMASS

The action of sodium chloride on collargol. A. F. GERASIMOV. *J. Russ. Phys. Chem. Soc.* **48**, 1848-51 (1916).—If a collargol soln. is coagulated by AcOH , and a NaCl soln. slowly added, the coagulated Ag at first redissolves and then, as the concn. of NaCl increases, is reprecipitated. This phenomenon is explained by the adsorption law, according to which adsorption is a function of ionic concn. It is assumed that at low concns., chloridion is more adsorbed than natrium, while, at higher concns. the reverse is the case. Thus, in the former case, a preponderating quantity of negatively charged chloridions is adsorbed by the discharged particles of Ag , which thus acquire a negative charge, and once again go into soln. When, however, the concn. of NaCl rises beyond a certain point, more natriums are adsorbed on the particles than chloridions, and their negative charge is again neutralized, causing them to be reprecipitated. J. C. S.

Effect of temperature changes on the viscosity of rubber colloids. RICHARD HAMER. *Proc. Am. Phys. Soc.* 1922; *Phys. Rev.* **19**, 552.—The viscosity of rubber sols in benzene was measured at 30° before and after temp. changes which consisted of cooling to 6° , in freezing solid at 0° , or at -190° by liquid air, or in heating to 60° . Cooling caused a slight increase in viscosity; freezing solid, a greater increase, and heating a slight increase. These results depended apparently on the variety and the concn. Successive applications appeared to have a cumulative effect, indicating, however, a limiting value. There was a slow recovery with time to the original or even a lower value. D. MACRAE

The electrolytic dissociation of ionogenic colloids. A. GYEMANT. *Kolloid-Z.* **33**, 9-15 (1923).—This is a theoretical treatment of the electrolytic dissociation of weak acids or bases which give colloidal dispersions in water, but whose salts are molecularly dispersed. F. L. BROWNE

The nature of the swelling process. VIII. Shrinking of cellulose acetate. E. KNOEVENAGEL. *Kolloidchem. Beihefte* **18**, 39-43 (1923); cf. *C. A.* **17**, 1568.— $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$ sol. cellulose acetate swelled in 50% EtOH increased in wt. 38.1% after 48 hrs. After standing during 6 months under water at room temp. the value was 36.2%. The 1.9% of shrinkage is beyond the limits of error. Similar expts. were carried out with cellulose acetate in alc.-benzene mixts. The degrees of shrinkage were much greater. K. maintains that swelling is always accompanied by simultaneous shrinking and that the two are reversible phenomena. Shrinking is small at room temp. but increases with rise in temp. or addn. of salts. I. NEWTON KUGELMASS

The study of soap solutions. J. W. MCBAIN. *Rept. Brit. Assoc. Advancement Sci.* 1922, 360-1.—In view of the great no. of theories which are irreconcilable with recent studies of soap solns., present evidence for the existence of the ionic micelle is outlined. C. C. DAVIS

The effect of concentration of the reacting solutions on the size of precipitating crystals. P. P. VON VEIMARN. *Kolloidchem. Beihefte* **18**, 44-76 (1923).—Polemical with H. Freundlich ("Kapillarchemie," 1923, p. 631), E. H. Buchner and J. Kalf (C. A. **14**, 2738) and W. Bancroft (C. A. **14**, 1625) on the theory of formation of cryst. ppts. and the quant. expression of the "law of corresponding states" of the process of crystn. I. NEWTON KUGELMASS

Four laws on the mutual influence of salts on their solubility. P. P. VON VEIMARN. *Kolloid-Z.* **32**, 145-9 (1923).—The well-known soly. law of Nernst does not hold for all concns. but should be worded: The soly. of a salt in the presence of another with a common ion decreases so long as the concn. of the 2nd salt does not exceed a certain limit. The 2nd law, of A. A. Noyes, that: The soly. of a salt increases in the presence of a 2nd salt which does not have an ion in common with the first salt, leads to a 3rd law, of V. that: The soly. of a salt in the presence of another with a common ion, increases when the concn. of the 2nd salt has reached a certain point at which substitution of the complex products formed by the dispersion medium takes place. Therefore V. introduces a

4th law that: When 2 or more substances are dissolved, then there is a combat for the solvent and the solv. of the less successful salt decreases. These deductions are from data in A. Seidell, "Solubilities of Inorganic and Organic Compounds" (New York 1919).

A. MUTSCHULLER

Solubility of nickel sulfate by floating equilibrium method. F. C. VILBRANDT AND J. A. BENDER. *Ind. Eng. Chem.* 15, 967-9 (1923); cf. *C. A.* 16, 2435.—The thermostats, thermoregulators and soln. app. are described. The solv. of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (green) and of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue and green) detd. by the method of floating equil. was in close agreement (slightly higher) with the results obtained by gravimetric methods.

H. M. McLAUGHLIN

The vapor pressures of saturated solutions of alums. STANISLAV MATZISHVSKII. *J. Russ. Phys. Chem. Soc.* 48, 1916-23 (1916).—The vapor-pressure curves for K and NH_4 alums are plotted, to see whether the empirical formula of Speranskii (*C. A.* 7, 3062) connecting vapor pressure, temp., and concn. of solns. is applicable to double salts. These curves consist each of two curves, intersecting, in the case of K alum at 79.5° and in the case of NH_4 alum at 82.7° , indicating that at these points chem. change of the alums occurs. Bertrand's formula connecting vapor pressure and temp. is not applicable to the curves for these two alums as a whole, but only to each portion separately. Speranskii's formula is not applicable to the K alum curve, and is only applicable to the NH_4 alum curve below 82.7° .

J. C. S.

The osmotic pressure of electrolytes. NIELS BJERRUM. *Z. anorg. allgem. Chem.* 129, 323-40 (1923).—The effect of interionic forces on osmotic pressure is shown to be a function of the concn. of electrolyte and of the ionic radius. In obtaining this function spherical ions with charges at the center were assumed. Individual differences shown by uni-univalent electrolytes even in dil. soln. (0.01 to 0.1 molar) are explained by difference in ionic size. From freezing point data ionic dimensions are calcd. on this theory. For the K, Rb and Cs halides the values so obtained agree with those from X-ray spectrographs. For Na, and especially Li and H, the values are significantly greater because of hydration. Ion radicals, as NO_3 , ClO_3 , BrO_3 , etc. have eccentric charges, seemingly near the surface of the ionic sphere, and this suggests a reason for the difference in osmotic effect of Cl and NO_3 .

A. E. STEARN

Researches on electrodiffusion—migration of ions. ALFRED GILLITT. *Compt. rend.* 177, 261-3 (1923).—Three % Na_2SO_4 in 10% gelatin was electrolyzed and sections of the gel were analyzed. The concn. curves of the NaOH produced at the cathode as well as the Na ion decrease at the anode corresponded to simple diffusion curves. Those for the H_2SO_4 and the SO_4 ion differ profoundly from diffusion curves. The velocity of the cation varies enormously with the current d., while that of the anion is not appreciably affected. After long electrolysis a sort of equil. at every point in the anode zone is reached when the anionic current seems to stop. This comes when 1 mol. of Na_2SO_4 disappears and is replaced by 2 mols. H_2SO_4 . There is a corresponding set of conditions at the cathode when 3 mols. NaOH replace 1 mol. Na_2SO_4 . This was not explained.

A. E. STEARN

Measure of the degree of ionization. ALLYRE CHASSEVANT AND CHOUCHAK. *Compt. rend.* 177, 133-5 (1923).—The degree of ionization, α , of mineral waters may be calcd. as a function of the cryoscopic point by the use of the equations: $\Delta_t = 1.85t \cdot C_m$ (Raoult) and $i = 1 + (K - 1)\alpha$ (Van't Hoff). C_m is the mol. concn. and K is the no. of ions formed by the total dissoc. of the mean mol., M_T , obtained by dividing the sum of the no. of ions by the mean concn. (cf. *Compt. rend.* 176, 1910-3).

H. M. McLAUGHLIN

Determination of the degree of dissociation of an electrolyte by the study of its conductivity. E. CHERBULIEZ. *Soc. Phys. Hist. Nat.* 39, 155-7 (1922); Suppl. to *Arch. des Sciences*, Nov.-Dec., 1922; *Science Abstracts* 26A, 415.—Hitherto from the cond. of an electrolyte in soln. it has only been possible to det. the degree of its dissoc. when the limiting mol. cond. at complete dissoc., λ_∞ , was known. Then the degree of dissoc. is known from the equation: $\lambda = \alpha\lambda_\infty$, $\alpha = \lambda/\lambda_\infty \dots (1)$, where α = degree of dissoc. as fraction of unity, λ = observed mol. cond. for a given concn., and λ_∞ = limiting mol. cond. For strong electrolytes λ_∞ may be detd. by measurements of the cond. of solns. more and more dil., which allow of extrapolation for infinite diln. Indirect methods are used for weak electrolytes. These obey the law of diln. For a binary electrolyte the law of diln. has the form $K = a^2/[v(1-a)]$, where K = dissoc. const. of the electrolyte, and v = vol. in l. contg. 1 g.-mol. of the electrolyte. On taking the logarithm of this equation and then differentiating and transforming, finally the following equation is reached: $a = (1 - 2 \tan \phi)/(1 + \tan \phi)$; $\tan \phi = d \log \lambda / d \log v$. From this by graphic representation of $\log \lambda$ as function of $\log v$, and drawing the tan-

gent at a point, a for this point may be obtained, and hence λ_{∞} . When the cond. is known to be about 35%, λ_{∞} may be detd. within some units %. When λ is represented as a function of $\log v$, concave curves are obtained with feeble dissoc., convex with high dissoc. The point of inflection corresponds with a dissoc. of 58.6% independently of the dissoc. const. of the binary electrolyte, provided it obeys the law of diln. It may be shown then that the tangent at the point of inflection $d\lambda_i/d \log v$ enables the value of λ_{∞} to be detd. by the following equation: $\lambda_{\infty} = [(3 + 2\sqrt{2})/\log 10] \cdot (d\lambda_i/d \log v_i) = 2.531 (d\lambda_i/d \log v_i)$. H. G.

Conductance of dilute aqueous solutions of hydrochloric acid. H. C. PARKER. *J. Am. Chem. Soc.* **45**, 2017-33 (1923).—The cond. of aq. solns. of HCl has been measured at 25° for concns. between 0.04 and 0.03 millimoles per l. Solns. were made up by wt. methods from water having a sp. cond. of 0.1×10^{-6} . Results show that values of previous investigators have been influenced by impurities in the water caused by the use of glass cells. Quartz cells were used in the present investigation. A variation in the cell const. is explained by adsorption of the electrolyte upon the electrode and a proper method of selecting the const. is detd. Λ_0 for HCl at 25° is 425.69, slightly higher than values previously obtained. Λ for the H ion at 25° is 349.89 ± 0.05 . The mass action const. is 0.195. C. R. PARK

Influence of small additions on the electrical conductivity of solid salts. C. TURBANDT and HERMANN REINHOLD. *Z. Elektrochem.* **29**, 313-7 (1923).—The increase in cond. of solid salts brought about by small additions of other salts is due to an increase in the mobility of the ions of the principal salt. The increase is not due to the formation of solid solns., for it occurs when both salts are non-miscible with one another in the solid state. H. JERMAIN CREIGHTON

The limits of hydrogen-ion concentration as determined by electrometric titrations in water solutions of carbon dioxide, calcium sulfate, and calcium carbonate. J. W. SIMPLEY and IVAN R. MCHAFFIE. *J. Soc. Chem. Ind.* **42**, 311-19T (1923).—Cast-iron pipes have been observed to corrode more rapidly in clay soils than in sand and gravel. These clay soils contain CaSO_4 . Clay soils in Canada, known to be corrosive, are highly calcareous. Corrosion is known to be a function of the H-ion concn. The possible variation of H-ion concn. in the presence of CaSO_4 and CaCO_3 was studied. The electrometric method was used in titration. Color indicators were also used. The p_H values obtained by the two methods agreed within 0.1. Readings obtained could be duplicated within 0.001 v. The temp. was maintained between 19 and 21°. In titration of $\text{Ca}(\text{OH})_2$ and CaCO_3 with CO_2 only one voltage drop was observed; thus no indication was given of the formation of bicarbonate. Similar results were obtained with Mg, Ba, and Sr, but in titration of KOH and LiOH the formation of bicarbonate was indicated. CaCO_3 suspended in H_2O was titrated with H_2SO_4 while CO_2 was passed into the liquid. Two voltage drops were observed, corresponding to the first addition of acid and the complete conversion to CaSO_4 . The p_H value of mixts. of CaCO_3 , CaSO_4 , and CO_2 was found to vary from 9.38, the value for satd. CaCO_3 alone, to 3.96 the value for satd. CO_2 alone. So long as all 3 substances were present the p_H value remained practically const. at 5.11. In the absence of CaSO_4 it did not fall below 6.56; hence the presence of CaSO_4 increases the acidity of water contg. CaCO_3 and CO_2 . In the absence of CaCO_3 the p_H value for satd. CO_2 was found the same whether CaSO_4 was present or not. H. B. GORDON

Concentration cells in non-aqueous solvents. A. N. SAKHANOV and A. M. GRINBAUM. *J. Russ. Phys. Chem. Soc.* **48**, 1794-1806 (1916).—The e. m. f. of concn. cells of AgNO_3 in pyridine soln. is investigated; it is for very small concns. of AgNO_3 (from 0.01 N to 0.0004 N) little different from that calcd. by Nernst's theory, or obtained with aq. solns. With greater concns., wide variations from theory are observed, owing to the formation of complex cations and to anomalous dissoc. The degree of dissoc. of AgNO_3 in pyridine soln. is calcd., and found to decrease rapidly as the concn. becomes greater than 0.1 N. Minimum dissoc. occurs with a normal soln., while at higher concns. the degree of dissoc. again increases owing to anomalies in dissoc. J. C. S.

Ghosh's theory of strong electrolytes. ADA PRINS. *Chem. Weekblad* **20**, 237-42 (1923).—A critical discussion of the theory, comparing actual exptl. results with figures deduced from Ghosh's postulates. Agreement is good, but the theory needs extension and modification. J. C. S.

The influence of neutral salts on the temperature coefficient of reaction velocity. F. O. RICE and WM. LEMKIN. *J. Am. Chem. Soc.* **45**, 1896-1900 (1923).—In continuation of previous work (C. A. **17**, 2529), the catalysis of the reaction between I and acetone was studied, with various acids as catalyzers, with and without the further addn. of salts. The results apparently contradict strongly the *radicalion theory*. Thus an

over 3-fold increase in reaction velocity with LiNO_3 was unaccompanied by any perceptible change in the temp. coeff. of the velocity. On the other hand, with H_2SO_4 as catalyst the addition of 0.434 mol. Na_2SO_4 hardly affected the velocity but lowered the temp. coeff. 2% in 2° , again contrary to the radiation theory, while with less H_2SO_4 both velocity and temp. coeff. were lowered. With strong acids "small quantities" of salt produced none or a small negative effect on the velocity, thus indicating that these did not diminish the dissociation of the acid, and that the strong acid was completely dissociated. The temp. coeff. of all strong acids is the same, and is unaffected by the presence of their salts. The temp. coeff. is lower the weaker the acid, and is considerably diminished by presence of salt with H_2SO_4 . W. P. WHITE.

In-, mono-, and divariant equilibria. XXIII. F. A. SCHREINEMAKERS. *Proc. Acad. Sci. Amsterdam* 26, 283-406 (1923).—A continuation of the previous paper (C. J. 17, 1745) in which the position of the P - T curves is discussed for the case when a new substance is added to a system in invariant equilibrium. The field in which the new curve of monovariant equilibrium lies is determined by the phases into which the new substance enters. E. D. W.

The bicarbonate equilibrium. J. W. SIMPLEY AND I. R. McHAFFIE. *J. Soc. Chem. Ind.* 42, 319-20T; 321-6T (1923).—From data obtained by electrometric titration of $\text{Ca}(\text{OH})_2$ with CO_2 and the soly. of CaCO_3 the hydrolysis of a satd. soln. of CaCO_3 is calcd. to be 8 or 10%. The value is much lower than those obtained by previous investigators. The soly. products of CaCO_3 and $\text{Ca}(\text{OH})_2$ at 20° were found to be 1.15×10^{-8} and 0.64×10^{-8} , resp. The const. for ionization of H_2CO_3 into H^+ and HCO_3^- was found to decrease with diln. while that for ionization of HCO_3^- into H^+ and CO_3^{--} increases with diln. and the product $\text{H}^+ \times \text{CO}_3^{--}$ is independent of diln. The proportion of dissolved CO_2 which is in the form of H_2CO_3 varies directly as the diln. H. B. GORDON.

The determination of compressibilities up to high pressures and applications to high-pressure chemistry. E. D. WILLIAMSON. *Rept. Brit. Assoc. Advancement Sci.* 1922, 359.—Compressibilities detd. at the Geophys. Lab. (Washington) are not accurate enough at the lower pressures; a method is developed involving a new form of *pycnometer* with which continuous readings can be made by a movable elec. contact. In studying the chem. effects of pressure on systems of more than 1 component, the compressibility of each soln. must be known to compute the vol. changes on which these effects depend. The vol. changes are calcd. from the slopes of the d. compn. curves. Even in a simple system (e. g., $\text{NaCl-H}_2\text{O}$) measurements in addition to compressibility, such as reliable d. compn. data at atm. pressure or some form of equil. dechis. (e. g., vapor pressure or c. m. f.), must be made. C. C. DAVIS.

The mechanism of reduction. I. H. J. PRINS. *Rec. trav. chim.* 42, 473-81 (1923).—The possible simultaneous chem. relations in a system of 3 components may be divided into 3 classes: (1) at least one of the components does not change either temporarily or permanently; (2) the 3 components influence one another in such a way that only temporary changes take place; (3) at least 2 of the components react with one another chemically. The 2nd class contains 2 cases in one of which A and B and A and C influence each other, in the other all 3 components influence each other. The third class contains 3 cases: (1) the case in which the reaction between A and B is catalyzed by the 3rd component acting as a catalyst; (2) the case in which 2 reacting mols. A and B are activated by the 3rd component C; (3) the case of 3 mols. reacting simultaneously. As the relation between the components changes with the temp. (an elevation of temp. increases their av. ant. of at. energy) a change in the temp. may move the system into another class. Thus a catalytic relation may change into a chem. one by raising the temp. Generally a reaction between 3 components is considered as a reaction consisting of 2 successive bimol. reactions. Yet the simultaneous collision of 3 components creates a much greater field of possibilities; the collision of 2 mols. gives rise to 1 possibility, but this no. increases to 3 for a trimol. collision and to 6 for a tetramol. collision. This illustrates the influence of a 3rd component. Instances of co-action between 3 components are much more numerous than is generally accepted; reduction and oxidation reactions in org. chemistry especially furnish examples. The preliminary expts. described in this paper are summarized by P. as follows: Reduction and oxidation of org. substances are often the result of co-action between the components, which react only through their combined action. Through this co-action it is possible to dissolve metals in a medium in which they are insol. as such, the co-action taking place between the undissociated mols. If Zn in the systems Zn-PhNO_2 and Zn-PhCO is replaced by more negative metals, e. g., Na, the PhNO_2 and the PhCO are able to disengage the metal atom from the cryst. compact and one may therefore suppose that in the case of Zn the reciprocal influence causes an activation. PhNO_2 is

strongly adsorbed on Zn, and reacts rapidly with the Zn and AcOH. PhNHOH is less strongly adsorbed, it reacts less rapidly and activates the surface of the Zn. PhNH₂ has no influence upon the H₂ evolution and is not appreciably adsorbed on the Zn. The adsorption is caused by the O atom, the latter being turned toward the Zn. II. *Ibid* 482-95.—The system Zn-PhNO₂-AcOH developed several interesting points and is treated extensively in this paper. The results of the expts. are given in the form of 17 graphs and discussed in connection with them. The expts. confirmed P.'s views concerning the relationship between chem. and catalytic activity. The reaction between Zn and PhNO₂ and AcOH proceeds so rapidly that the reaction between the H⁺ ions and Zn cannot profit by the temporary activation of the Zn surface around the adsorbed PhNO₂ mols. If the NO₂ group is replaced by the less active NHOH group of PhNHOH the opportunity for the reaction between H atoms and Zn to profit by the activated condition of the Zn atoms is much greater, because of the fact that the av. life of the NHOH group upon the Zn surface is considerably greater than that of the NO₂ group. PhNH₂, which does not contain the active group which may react or become adsorbed by the Zn, has no influence at all. It is to be expected that there are substances which activate the Zn without being reduced to a perceptible degree. The replacement of an active group like the NO₂ group by a less active one produces an activation which is in accordance with P.'s theory concerning the relationship between chem. activity and catalysis (*C. A.* 8, 2762). Examples of the same kind are the following: If H₂SO₄ reacts with a substance A, one may expect an activation of A as long as the energy corresponding to the loss of potential energy between the components is not dissipated throughout the system but accumulated in the neighboring atoms. The time of relaxation will be less, when the amt. of energy converted is greater. In this case the chance for a catalytic action between the substance A and a 2nd one B will be much less than the chance of a reaction with the formation of a stable compd. between H₂SO₄ and A. If the H₂SO₄ is replaced by a less active acid, e. g., a sulfonic acid, the conditions for a catalytic action will be much more favorable. Furthermore the chance to form a stable compd. will be less if the 2 components differ widely in chem. character or polarity. When the NO₂, the NHOH and the NH₂ groups are compared, it appears that the 1st gives rise only to a chem. reaction as well as an activation, whereas the last is catalytically as well as chemically inactive. These 3 groups give a striking example of the 3 possible relations between chem. compds. as treated several years ago by P. (*C. A.* 8, 3656). At the same time an indirect proof was obtained of the groups in the interface between Zn and AcOH. The decreasing activity in the series NO₂, NHOH, NH₂ makes it very probable that the unsatd. O₂ atom is the cause of the adsorption on the metal surface; the mols. are turned with their Ph groups to the AcOH. This confirms the view of P. that the direction of adsorption is detd. by the unsatn. of the atoms (having the largest amt. of at. energy) and by the contrast (which coincides with the greatest lateral distance between their places in Mendelejeff's table and with the greatest difference in the character of the outer electrons). The fact that the O₂-contg. group is oriented towards the Zn instead of towards the AcOH also shows that the adsorption is directed by other factors than the soly. If these 2 were identical the O₂-contg. group should turn towards the O₂-contg. AcOH. The orientation is not caused by the similarity in polarity (as proposed by Harkins), nor does it coincide with the direction detd. by the soly. (as proposed by Langmuir), because in both cases the O₂-contg. group would then be turned towards the AcOH.

E. J. W.

The mechanism of catalysis. H. W. UNDERWOOD, JR. *Chem. Met. Eng.* 29, 584-7 (1923).—An account of the present status of the subject with special emphasis on the industrial side.

E. J. C.

The catalytic decomposition of hydrogen peroxide in a bromine-bromide solution. II. Rate measurements in dilute solutions and in the absence of sulfate, and their interpretation as a function of the activity product of hydrobromic acid. R. S. LIVINGSTON AND WM. C. BRAY. *J. Am. Chem. Soc.* 45, 2048-53 (1923); cf. *C. A.* 17, 2220.—The steady-state rate of the bromine-bromide catalysis of H₂O₂ has been measured in dil. solns. of H₂SO₄ and KBr. The rate const. approaches a definite value as the H₂SO₄ is indefinitely increased. The steady-state rate was also measured in solns. of HBr, HBr-HClO₄, HBr-KBr, HBr-BaBr₂ and HClO₄-KBr. At the steady state in a majority of the expts. the rate of decomp. of peroxide is represented within the limits of exptl. error by the expression $-d(\text{H}_2\text{O}_2)/dt = 0.0437(\text{H}_2\text{O}_2)(\text{H}^+)(\text{Br}^-)^{-1/2}\text{HBr}$. The activity coeff. of HBr in solns. contg. H₂SO₄ and KBr has been estd. from the rate measurements in these solns. by the assumption that this equation holds. The application of the "activity-rate" theory and of Brønsted's theory to the expts. is briefly discussed.

L. T. F.

The mechanism of oxidation of charcoal. O. MEYERHOF and H. WEBER. *Biochem. Z.* 135, 558-75(1923); cf. Warburg, *C. A.* 16, 1436.—The degree of self-oxidation of charcoal in alk. soln. depends on the source of the charcoal (probably on the adherent, oxidizable impurities), the partial pressure of O_2 , and the temp. The ratio by vol. of CO_2 produced to O_2 consumed lies between 0.5 and 1.0; utilization of 1 cc. O_2 produces 4 cal. The phenomenon is a *surface catalysis*, since it is inhibited by urethans and the extent of inhibition varies with the degree of adsorption of the different urethans. When $[OH]$ is const., the degree of oxidation increases in the following order: alkali hydroxides < alk.-earth hydroxides < $AgOH$, < $C_2H_5NH_2OH$, and is thus dependent on the extent of hydroxyl ion adsorption. With the exception of glucose phosphoric acid, the carbohydrates are not appreciably oxidized.

GEORGE ERIC SIMPSON

The behavior of activated sugar carbon in contact with hydrogen peroxide solution. J. B. FIRTH and F. S. WATSON. *J. Chem. Soc.* 123, 1750-5(1923).—A study of the decompn. rate of H_2O_2 in soln. in the presence of sugar carbon yielded the following conclusions: Ordinary sugar carbon gives rise to a very slight decompn. Sugar carbon heated for two hrs. *in vacuo* at 600° shows greater activity. A considerable increase is manifested by carbon which has previously sorbed I from soln. and from which the I has been removed. The activity of the carbon gradually decays during the decompn. of the H_2O_2 . The vol. of O liberated is in a general way proportional to the amt. of C used. The activity of the carbon increases rapidly with rise of temp. C. R. PARK

Oxide equilibria in catalysis. J. M. WEISS, C. R. DOWNS and R. M. BURNS. *Ind. Eng. Chem.* 15, 965-7(1923).—A study was made of the compn. of the V oxide catalyst used in the oxidation of C_6H_6 and of the effect on the oxide equil. of varying the benzene-oxygen ratio. The compn. of the V oxide at a given temp. and pressure depended on the air-benzene ratio used. The behavior of the catalyst strongly suggested that the mechanism of the reaction involved an oscillation between V_2O_3 and V_2O_4 . The proportion of complete combustion was not dependent on the ratio $V_2O_3 \div V_2O_4$. The productivity of the catalyst, whether oxides of 1 or more metals, seemed to be a function of some undetd. property other than the activation of the O by dissociation of the oxide. In the oxidation of naphthalene, anthracene and methylbenzenes, the no. of catalysts which produced partial oxidation products progressively increased with the complexity of the mol.

H. M. McLAUGHLIN

Catalytic actions at solid surfaces. XI. The action of alumina and certain other oxides in promoting the activity of nickel catalyst. R. F. ARMSTRONG and T. P. HILDRITCH. *Proc. Roy. Soc. (London)* 103A, 586-97(1923); cf. *C. A.* 17, 2220.—The addn. of small quantities of Al_2O_3 , Fe_2O_3 , MgO or SiO_2 to Ni increases its activity as a hydrogenation catalyst. The stimulating effect of these oxides, which are not reduced during hydrogenation, is attributed to the increased Ni surface made available by their mech. supporting action.

J. A. ALMGUIST

Constitutional diagram for the system silver nitrate-mercuric iodide. I. A. G. BERGMAN. *J. Russ. Phys. Chem. Soc.* 53, 181-92(1921). The system was studied thermally with a copper-constantan couple and a self-registering pyrometer of Kurnakow calibrated from freezing curves of *o*-nitrophenol, naphthalene, benzoic acid, hydroquinone $AgNO_3$, Sn. The particular fields and points of the diagram are: (1) $AgNO_3$, m. 208° , transformation p. 160° ; (2) solid soln. up to 7.4 mol. % HgI_2 with a complete eutectoidal transformation at 134° ; (3) first eutectic point at 20% HgI_2 and 78° ; (4) solid soln. from 22% to 33.3% HgI_2 at 78° ; its range narrows down at the $AgNO_3$ side at lower temps.; (5) first compd., $HgI_2(AgNO_3)_2$, m. 107° , greenish yellow crystals, no polymorphic changes; (6) second eutectic appears between 33.3 and 50.0% HgI_2 ; (7) second eutectic point at 41.5% HgI_2 and 92° ; (8) second compd., $HgI_2 \cdot AgNO_3$, m. $117-8^\circ$, polymorphic change at 52° , the latter being lowered continuously by the presence of the first compd. down to 48° ; color canary-yellow above the transformation point, orange-yellow below it; (9) third solid soln. range 50.0-53.5% HgI_2 , stable at low temps.; transformation point lowers down to 45° at the solid soln. limit; (10) third eutectic range 52-92% HgI_2 ; (11) eutectic point, 58% HgI_2 and 108° ; (12) fourth solid soln. 92-100% HgI_2 , stable at low temps.; one transformation point due to HgI_2 is raised continuously by the presence of $AgNO_3$ to 138° ; (13) HgI_2 , m. 259° , transformation point 127° . M. G. KORSUNSKY

Ternary system aluminium-zinc-tin. II. Binary system aluminium-zinc and ternary system zinc-aluminium-tin. E. CREPAZ. *Giorn. chim. ind. applicata* 5, 285-90(1923); cf. *C. A.* 17, 2220.—Diagrams and tables are given on the following topics: (1) fusion of Al-Zn mixts., (2) fusion of Al-Zn-Sn mixts., (3) isotherms of solidification of Al-Zn-Sn mixts. The ternary eutectic is practically free of Al and is identifiable with the binary Sn-Zn eutectic. The decompn. of the solid soln. β is favored by the presence of Sn. Some photomicrographs are given.

ROBERT S. POSMONTIER

Relations of the potential surface of the ternary alloys of cadmium, mercury and tin or lead. ROBT. KREMAN, HERMANN PRAMMER AND LUDWIG HELLY. *Z. anorg. allgem. Chem.* 127, 295-315(1923).—A detailed study has been made at 25° of the potential relations existing in the 2 ternary systems Cd, Hg, Sn and Cd, Hg, Pb. Iso-potential diagrams have been drawn for both systems. The relation of the potential conditions to the phases existing in various parts of the system is discussed in detail.

C. R. PARK

The binary system, tungsten-molybdenum. W. GEISS AND J. A. M. VAN LIEMPT. *Z. anorg. allgem. Chem.* 128, 355-60(1923).—Small rods were prepd. by pressing and sintering powder of the very pure metals in various proportions. The current strength required to fuse these in an atm. of H_2 was detd. From the measured black temps. the fusion curve was calcd. A practically straight line resulted, indicating a continuous series of mixed crystals. As a check the temp. coeff. of elec. resistance was detd. and plotted for alloys in various proportions. A continuous curve resulted. The temp. coeff. is a good means to det. quant. the Mo content of otherwise pure W. One wt. % of Mo lowers the temp. coeff. about 10%. The alloys have a resistance less than 60% above that of the pure components. The small effect of Mo in lowering the cond. of W is very striking in comparison with Au-Ag or Au-Cu alloys.

A. R. M.

Solubility between cadmium and thallium in the solid state. CLARA DI CAPUA. *Atti accad. Lincei* [v] 32, i, 282-5(1923); cf. Kurnakov and Pushin, *J. Russ. Phys. Chem. Soc.* 33, 565-88(1901); Bornemann, *Metallurgie* 7, 103(1910).—The author has investigated the diagram of state of Cd-Tl alloys by Plato's method (*Z. physik. Chem.* 55, 721-37(1906); 58, 350-72(1907)). The eutectic corresponds with about 1.82% of Tl, and the initial solidification curve closely resembles that given by Kurnakov and Pushin, but different results are obtained insofar as the extension of the eutectic horizontal is concerned. On the Cd side, the annulment of the eutectic arrest corresponds virtually with the pure metal, while on the Tl side the eutectic arrest is annulled at a concn. of about 2.5% of Cd; thus appreciable soly. of Tl in Cd is excluded, whereas Cd is slightly sol. in Tl in the solid state. The results of cond. and cryoscopic measurements are in agreement with these conclusions.

J. C. S.

The determination of boiling points by distillation from test-tubes. A. K. BOLDUK-REV. *J. Russ. Phys. Chem. Soc.* 48, 1862-70(1916).—A slight modification of the method described by Pavlevski (*Ber.* 14, 88) for the detn. of the b. p. of small quantities of substances. A small test-tube, provided with a side-tube, and a cork through which a thermometer passes, is wrapped around with asbestos, and fits into an aperture cut in a sheet of the same material. The lower end of the tube which protrudes through the asbestos sheet is heated with a naked flame until the contents boil. The thermometer reading at first rises, then remains const. for some time, this temp. being taken as the b. p., and then again rises, owing to superheating. The best results are obtained by keeping the bulb of the thermometer at least 4 cm. above the level of the liquid, so as to avoid the spattering of the superheated liquid. By this method triphenylamine gave b. p. 364.8° (corr.). Its soly. in 100 g. of EtOH and of MeOH is measured, and is in the former solvent 0.74 g. at 19-20.5°, and 5.5 g. at 74°, and for the latter 0.73 g. at 19-20.5°, and 3.3 g. at 65°.

J. C. S.

Calculation of flash points for pure organic substances. EDWARD MACK, C. E. BOORD AND H. N. BARRHAM. *Ind. Eng. Chem.* 15, 963-5(1923).—The flash points of pure liquid and solid org. compds. can be calcd. when their vapor pressures are known in the region of the flash point temp. According to Thornton (*C. A.* 11, 1904), in a mixt. of air and a combustible gas or vapor, the min. explosive mixt. contains about twice as many O atoms and the max. mixt. about $\frac{1}{2}$ as many O atoms as are required for complete combustion. This rule has been used to calc. the flash points of aliphatic and aromatic hydrocarbons, phenols, aliphatic esters, and alcs. This may be done by calcg. from vapor-pressure data the temps. to which the substances in question must be brought in order that their satd. vapors will furnish mixts. with air which are just explosive. Flash points calcd. in this way agree well with exptl. values.

C. T. WHITE

The melting point of ice on the absolute temperature scale. L. B. SMITH AND R. S. TAYLOR. *J. Am. Chem. Soc.* 45, 2124-8(1923).—The value of the abs. temp. of melting ice from the vol. coeff. of N_2 is found to be 273.159° and from the pressure coeff. 273.097°. The mean value obtained by using the data of other gases including the Joule-Thomson coeff. is 273.13° \pm 0.01°.

F. L. BROWNE

Variation of the specific heat of gases with temperature according to the most recent researches. H. MURAUER. *Chimie et industrie* 10, 23-9(1923).—A critical review giving examples of the applications of the values found. A bibliography is given.

A. PAFINEAU-COUTURE

Specific heat of solids at high temperatures and the quantizing of oscillations of finite amplitude. E. SCHRÖDINGER. *Z. Physik* 11, 170-6(1922); *Science Abstracts* 26A, 280.—Recently Born and Brody (*C. A.* 16, 1693) have developed a theory of the sp. heat of solids at high temps., the chief result of which is their conclusion that deviations from Dulong and Petit's law at high temps. are to a first approximation proportional to the abs. temp. This result is proved on the quantum theory, and the authors point out that the same result can be obtained on the classical theory, but that it is not simpler (cf. *C. A.* 16, 1695). S. disagrees with this latter statement, and gives a mathematical proof based on Hamiltonian functions for a mech. system. H. G.

The theory of specific heat advanced by Debye. RUDOLF MEYER. *Z. Samerstoff. Stickstoff. Ind.* 14, 93-5; *Chem. Zentr.* 1922, 111, 1279; cf. *C. A.* 17, 1367. The theory advanced by Debye (cf. *C. A.* 7, 2891) for sp. heat is valid neither for low nor for high temps. Expts. of von Heylandt on the decrease in vol. of O and of air at the b. p. show that this decrease follows with lowering temp. the exponential formula derived by M. C. C. DAVIS

The specific heat of mixtures of aqueous solutions of sodium chloride and cane sugar. (Miss) H. BLASZKOWSKA. *Bull. soc. chim.* 33, 562-71(1923). Doroshewskii had found (*C. A.* 17, 2984) that several properties of certain mixts. of solns. followed the mixts. rule. This fact was described by saying that "the solvent divided itself among the solutes in proportion to the no. of gram-equivs. of these." Miss B. tests this rule for sp. heat, and for d , including more concd. solns. than D had used. Duplicate calorimetric observations agreed, on the whole, to better than 1 per mille; D's rule was confirmed to a little better than 3 per mille, which was said to be as good as the observations. But 3 per mille is from 3% to 6% of the change in the sp. heat of water produced by dissolving the NaCl in it, and about the same % of the difference in the sp. heats of the two solns. W. P. WHITE

The heats of vaporization of mercury and cadmium. M. F. FOHLER AND W. H. RONGBUSH. *J. Am. Chem. Soc.* 45, 2080-90(1923).—The importance of a knowledge of the entropies of the monatomic gases is emphasized. An attempt to apply the steam calorimeter principle to Hg failed, probably through the great activity of radiation. Hg was then vaporized electrically in a vapor bath of dibutyl ether at 112°. The max. variation between results was 5% but the systematic error of the av. is probably less than this. The heat of vaporization of Hg at 112° is put at 14,490 \pm 50 cal., corresponding to 14,670 at 298° K., against 14,615 cal. from Smith and Menzies' empirical equation. The result with Hg indicated that vapor-pressure data could be well used to give heat of vaporization. Hence for Cd the vapor pressure was detd. by finding the b. p. at pressures from 80 mm. to 10 mm., in an app. much like a sulfur b. p. app. The data, together with Wüst, Meuthen, and Durrer's value for the sp. heat of liquid Cd, give at 591.1° K., $\Delta H = 25,350 \pm 100$ cal. The entropies of the vapors at 298° K. and 1 atm. are Hg, 41.41, Cd, 39.90, agreeing to better than 3 per mille with predictions by G. N. Lewis. W. P. WHITE

The heat of formation of solid solutions. G. BRUNI. *Bull. soc. chim.* 33, 696-7 (1923). Reply to the preceding note. Ph. LANDRIEU. *Ibid* 697-9. The heat of formation of solid solutions. G. BRUNI. *Ibid* 907-8.—L. had stated that the heat of formation of solid solns. was very small, but very little investigated. B. calls attention to several researches, some showing appreciable heat, positive or negative. L. points out that these cases were not fair tests of the rule, for various reasons. B. recalls that in one case he had called attention to a connection between large heat formation and novelty at ordinary temps. W. P. WHITE

The significance of induced polarity. J. KENNER. *Rept. Brit. Assoc. Advancement Sci.* 1922, 358-9.—Lapworth's derivation of the principle of induced alternate polarities (cf. *C. A.* 16, 2048) is a further development of the views of Werner and Plüschheim with the aid of postulates which conform to the thermodynamic condition for the attainment of stable equilibrium. Fry's electronic valence theory rests on the fallacy that 2 atoms in direct combination necessarily have opposite polarities. Observed results are explicable by assuming that polarity depends upon a constraint of the mol. (due to the formation of mol. compds.) and that of 2 alternative reactions, that one will predominate in which the free energy gradient is the greater. Therefore, before a reaction can be predicted the point of constraint must be known. This is detd. by steric considerations or by the nature of the reacting compds. The practice of labeling atoms, + or — is correct only insofar as it shows the condition they tend to assume. The key atom in a mol. is the point at which constraint originates. It is suggested that a more complete conception of chem. reactions can be obtained by studying the lines of force associated with the electrons. It is emphasized that the intermediate production of

induced alternate polarities represents only 1 course by which equil. is attained, and a reaction may take a course not anticipated by the ordinary application of + and - notation.

C. C. DAVIS

The unipolar conductivity of metal sulfides. G. G. URAZOV. *J. Russ. Phys. Chem. Soc.* 51, 311-52(1919).—The metal sulfides present large variations in their relations to the elec. current. Their conds. vary from the purely metallic type, decreasing with the rise in the temp., to the electrolytic type increasing with the temp. U. endeavored to obtain exact data concerning the *electric properties of Ag_2S and Cu_2S* , by using synthetic sulfides, melted in graphite crucibles and cast in glass tubes. The rods so obtained were annealed at about 300° for the purpose of normalizing the structures and the conds. Ag_2S has a cond. which may be represented by a formula $\lambda_t = \lambda_0 e^{\alpha t}$, where λ_0 varies from 0.000293 to 0.000315, and α from 0.049 to 0.052. The presence of a very small excess of Ag brings λ_0 to a much higher figure, while α becomes greatly lowered. Samples made by extruding Ag_2S through a die also possess a higher λ_0 and a lower α . The actual values depend upon the state of Ag_2S , which seems to undergo a change from α to β somewhere between 70° and 105°. The well known transformation at 175° from β to γ leads to an enormous increase in cond. (1.99 at 170° to 21.30 at 175°). "Resistance of trespassing" does not exist. D. c. produces an enormous decrease of the resistance. This decrease is an asymptotic function of time of the d. c.'s action; hence the resulting final resistance is about 0.27% of the initial. Decrease in resistance is accompanied by the appearance of a counter e. m. f. of about 0.150 v. in the beginning, asymptotically falling to 0.003 v. The action is certainly electrolytic. Homogeneous and strictly stoichiometric samples of Cu_2S were difficult to obtain. This resulted in very variable figures for λ_0 (0.041 to 0.00518 in the α state) while the figures for α were comparatively stable (0.015 to 0.0165). In the β state λ_0 varied from 0.0099 to 0.339, and α from 0.00707 to 0.0162. The transformation $\alpha \rightarrow \beta$ begins above 84° and ends below 98°. This interval is caused by variations in compn. The cond. of Cu_2S is enormously increased by the presence of excess S, which enters solid solns. with Cu_2S . 1% S raises the cond. many thousand fold. Temp. uniformly adds to this increase up to 90° and above 190°. In the interval 90-190° cond. drops heavily as a result of the α to β transformation, which proceeds continuously because of the action of S. D. c. produces in the α state an increase of cond. and a counter e. m. f. (of 0.078 v. at the beginning, 0.093 v. to the end), both being, however, very complicated functions of time of action. In the β state the cond. drops steeply under the action of d. c. at the beginning, then the drop becomes less pronounced. The counter e. m. f. also drops steeply in the first few min., then remains almost const. at 0.057 v., and finally drops steeply to 0.006 v. The action of d. c. is purely electrolytic. The thermoelec. force of Cu_2S against Cu was detd. for 3 samples. Those most nearly coinciding in compn. with the pure Cu_2S give the highest force, averaging 0.75 mv. per 1°, with a break at the temp. of α to β transformation. Excess of both Cu and S blurs the transition point and lowers the thermoe. m. f. considerably.

M. G. KORSUNSKY

Effect of the electrostatic charge of gas bubbles evolved electrolytically. ALFRED COEHN. *Z. Elektrochem.* 29, 308-8(1923).—An address. H. JERMAIN CREIGHTON

The Hall effect in anisotropic rectangular laminæ. E. PERSICO. *Atti accad. Lincei* 31, II, 500-4(1922); *Science Abstracts* 26A, 303.—Assuming ions + e and - e, and replacing the scalar mobility by a tensor proper to each class of ion, the equations are worked out. An equiv. image-plane is found. The same results can be obtained with a rectangular isotropic lamina of a different form. The difference between the observed Hall effects when transversal or longitudinal is not a proper Hall effect difference; but it is a difference between the perturbations introduced by the electrodes, which difference tends to vanish as the lamina is lengthened in the direction of the current. With point electrodes in a long lamina, the same coeff. would be obtained with the current parallel or transverse to the axis, both in isotropic and anisotropic laminæ.

H. G.

Dynamic characteristics of helium arcs. FABIAN M. KANNENSTINE. *Proc. Am. Phys. Soc.* 1922; *Phys. Rev.* 19, 540.—He arcs were formed by impressing a 60-cycle alternating e. m. f. between a Wehnelt cathode and nickel plate in a pyrex tube contg. pure He. The relation between the e. m. f. impressed and the current through the arc was obtained by Braun tube oscillograms. The arc struck at about 21 v. and the current through the arc increased in much the same way as found by Compton, Lilly, and Olmstead (*C. A.* 15, 14). However, as the voltage decreased quite different results from theirs were obtained. The decreasing part of the curve was above the increasing part and formed a loop, while the arc, instead of breaking at 20 v., broke at or near 0 v. The decreasing curve instead of being smooth had 2 sudden changes in curvature, one at

or near zero and the other considerably higher but below the striking potential. These curves seem to indicate that in the arc products are formed which have a very low ionization potential and a short but measurable life period.

The magneto-chemical effect. A. N. SUCHUKAROV. *J. Russ. Phys. Chem. Soc.* **48**, 1785-83 (1916); cf. *C. A.* **10**, 2830.—BaCl₂ soln. is electrolyzed in a strong magnetic field. A stream of positively charged particles emanates from the region of the soln. where liberation of ions takes place. These particles move with great velocity, as they are able to penetrate a layer of soln. 1 cm. in thickness, the min. penetrative power observed being half as great. The nature of these particles is not certain, but it seems possible that they are produced as a result of the disintegration of the Cl atom. A platinum-platinoidium thermoclement placed in the soln. within range of the particles gives a perceptible heat effect, so that they appear to possess considerable kinetic energy. A stream of negatively charged particles is also observed, but these have not up to the present been investigated.

Diamagnetism and chemical constitution. P. PASCAL. *Rev. gen. sci.* **34**, 388-99 (1923); cf. *C. A.* **3**, 2899; **4**, 553, 1838, 2007; **5**, 2217, 6, 2599, 2710; **7**, 18, 1325, 3071, 3913; **8**, 1385, 3150; **9**, 17.—In review of previous work some of the data have been slightly changed. The at. susceptibility, (χ_A) = $K \times 10^{-7}$, is for H, -29.3 (no. for K is given); F, -61; Cl, -201; Br, -306; I, -416; S, -150; Se, -235; Te, -378; N, -55.5; C, -60. These values calcd. on the basis of the additive law are in good agreement with exptl. results. Combined O as shown by the following values for K is diamagnetic except for aldehydes, ketones and nitroso derivs. For -O- in alics, ethers and hydroxides K is -46; O= in aldehydes and ketones, +17.5; O= in amides, -15; O₂ in acids and esters, -79.5; O= in nitroso derivs., +39.5; O₂ in nitrates, -31.5. The mol. susceptibility for A_aB_bC_c... is calcd. by $\chi_M = \sum a\chi_A + \lambda$. The const. λ = $K \times 10^{-7}$ for =C=C= (ethylene) is +51.5; =C=C= (allyl) +45; -C=C-, +8; -N=N-, +18.5; =C=N-, +81.5; -C=N-, 8; 2 × (C-C), +105.5; 2 × (C=C), +16; 2 × (C=N), +102; N-nucleus, +10; hexamethylene chain, +30; benzene nucleus, -14.5; naphthalene nucleus, -81. Two important regularities in the at. susceptibilities are shown graphically and the suggestion is made that these may be useful in developing the electronic theory of matter: (1) When the at. wts. of the diamagnetic elements are plotted with the log (χ_A) , the curve breaks periodically at the points which correspond exactly with the elements of the same family, thus S, Se and Te form minima; Cl, Br, I, P, As, Sb and Bi form maxima, etc. (2) For any family of the periodic table, the log of the at. susceptibilities is a linear function of the at. no. (N), $\log (-\chi_A) = \alpha + \beta N$, where β is a function of valence. The additive law for diamagnetic properties is used to det. the structure of the acids of N, I, S and P. The susceptibility of the nitroso group, -N=O is -16×10^{-7} , of the NO₂ in metallic or org. nitrites is -56×10^{-7} . The difference corresponds to the at. susceptibility of O in alc., i. e., to the formula, O=N-OH, for nitrous acid. By similar values, iodic acid has the structure, IO₂OH; sulfuric, SO₂(OH)₂; thiosulfuric, S₂O₂(SH)(OH); dithionic, SO₂(OH)-SO₂(OH); polythionic acids, SO₂(OH)-S_n-SO₂(OH); sulfurous, SO(OH)₂; hypophosphorous, PH(OH)₂; phosphorous, P(OH)₃; phosphine oxides, O=P(OH)₃;

phosphonic, R-P(=O)(OH)₂; phosphoric, O=P(OH)₃.

H. M. McLAUGHLIN

The magnetic properties of gadolinium ethylsulfate at low temperatures. L. C. JACKSON and H. K. ONNES. *Compt. rend.* **177**, 154-8 (1923); cf. *C. A.* **8**, 863, 2090.—Gd₂(SO₄)₃·8H₂O is strongly paramagnetic and obeys the law of Curie to the lowest temps. observed. Measurements of the magnetic susceptibility of this substance were made upon the cryst. powder. In order to det. the susceptibilities along the 3 principal magnetic axes it was necessary to use individual large crystals. The crystals of Gd₂(SO₄)₃·8H₂O were much too small to serve for this purpose. The authors substituted Gd ethylsulfate, large crystals of which were available. Measurements of the magnetic susceptibilities of the crystals of Gd ethylsulfate were made for numerous orientations of the crystal. The susceptibilities thus measured for different axes did not differ from the av. susceptibility by more than 1 part in 1000. The av. susceptibility was detd. with the substance in powd. form. The 3 principal susceptibilities are shown to be equal at every temp. since they all obey the law of Curie— $\chi T = \text{const.}$ where χ = magnetic susceptibility and T = abs. temp. The crystals of Gd ethylsulfate are magnetically isotropic.

L. M. HENDERSON

The optical properties of leguminates of the alkali metals. M. A. RAKUZIN and G. F. PEKARSKA. *J. Russ. Phys. Chem. Soc.* **48**, 1888-9 (1916).—Various optically active alkali metal leguminates have been prepd., and their optical rotations measured:

the NH_4 salt has $[\alpha]_D -67.33^\circ$, the Li salt, $[\alpha]_D -38.86^\circ$, the Na salt, $[\alpha]_D -39.31^\circ$, and the K salt, $[\alpha]_D -39.62^\circ$. The low values obtained for the last 3 salts are undoubtedly due to racemization, but a gradual increase in the optical rotation is observable with increasing at. wt. of the metal.

J. C. S.

The structural significance of optical rotatory quality. J. LARMOR. *Repts. Brit. Assoc. Advancement Sci.* 1922, 351.—A mathematical discussion of the function of crystal form in producing optical rotation (cf. C. A. 16, 1902). Since quartz exhibits high optical rotation in crystal form but none when fused, the optical activity must be due to chirality in the crystals which is not present in the constituent mol. A mol. may thus be chiral geometrically without being chiral in optical structure.

C. C. DAVIS

The turbidity points at constant temperature. H. GAULT, W. STRINKHLER AND A. SCHAEFFER. *Mit. grasses* 14, 6052-8(1922).—Five methods are reviewed for detn. of *iscater in oils*. The following systems were investigated with the turbidity point as an indicator: (1) $\text{NaCl-H}_2\text{O-C}_2\text{H}_5\text{OH}$; (2) benzene- $\text{C}_2\text{H}_5\text{OH-H}_2\text{O}$; (3) $\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$; (4) $\text{Me}_2\text{CO-benzene-H}_2\text{O}$; (5) $\text{C}_6\text{H}_6\text{-Me}_2\text{CO-H}_2\text{O}$ and (6) spindle oil- $(\text{C}_2\text{H}_5)_3\text{NII-H}_2\text{O}$. Data are given in curves and tables.

ARTHUR L. DAVIS

Diagrammatic motion slides. BROTHIER GABRIEL. *Can. Chem. Met.* 7, 233-4 (1923).—A description of a new method of illustrating chem. principles by producing a controlled motion-picture effect with special projection app.

E. J. C.

Aluminium hydroxide. I. Hydrates and hydrogels (WILLSTÄTTER, KRAUT) 11A. Adsorption of compounds and quantitative analysis (DHAR, *et al.*) 7. The anode effect (ARNDT, PROBST) 4.

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3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The hydrogen molecule. H. S. ALLEN. *Nature* 112, 310-1(1923).—A H mol. in which the electrons are at rest instead of in orbital motion is postulated. The static model is obtained by endowing the nucleus or electron with a "magnetic wheel." A quantum force of the kind introduced by Langmuir exerts repulsion or attraction according to the sign of the elec. charges between which the force acts. Hence in addition to the electrostatic force, e^2/r^2 , there exists a quantum force $F = e^2 a_{\text{ext}}/r^2$, which is repulsive for unlike charges, but attractive for like charges. For the various models the following data are calcd.: neutral H mol., (1) θ (angle between the line joining nucleus and electron and the line joining nuclei) = 45° , d_1 (distance between nuclei in 1-quantum state) = 0.871 \AA. , I_1 (moment of inertia in C. G. S. units) = 6.261 , W (work required for complete dissociation) = 30.06 v. ; (2) $\theta = 60^\circ$, $d_1 = 0.584$, $I_1 = 2.818$, $W = 29.68$; (3) $\theta = 30^\circ$, $d_1 = 1.012$, $I_1 = 8.453$, $W = 29.68$; ionized mol., $d_1 = 1.239$, $I_1 = 12.66$, $W = 17.34$; triatomic mol., $I_1 = 9.726$, $W = 46.25$ (nuclei and electrons at alternate corners of hexagon with side length of 0.625 \AA.). G. L. CLARK.

Structure of the molecules. A. P. JENKIN. *Nature* 112, 326(1923).—In an attempt to reconcile static and dynamic conceptions of at. and mol. structure, the suggestion is made that when an electron is shared by 2 atoms as a result of chem. combination, it continues for the moment its revolution but in a new plane and finally becomes stationary. A diagram of tartaric acid constructed upon this scheme is given.

G. L. CLARK

Radium minerals of Belgian Congo and their treatment in Belgium. ALFRED SCHOEP. *Chimie et industrie* 10, 167-9(1923).—Brief description of the minerals and their occurrence with an outline of the commercial process for obtaining the Ra at the Oolen plant (Belgium). It consists essentially in grinding, treatment with acids to eliminate U, Fe, Cu and P_2O_5 , treatment with NaCl soln. to remove Pb, treatment with HCl to remove Ca, treatment with Na_2CO_3 to eliminate H_2SO_4 . The Ra is then dissolved in HCl, pptd. as sulfate, transformed into carbonate and then into chloride, and finally sepd. from the Ba (about 125,000 of Ba to 1 of Ra) by a series of fractional crystals, first in H_2O , then in HCl and finally in HBr soln.

A. PAPINEAU-COUTURE

Photographing the disintegration of an atom, and a new type of rays. W. D. HARKINS and R. W. RYAN. *J. Am. Chem. Soc.* 45, 2095-107(1923).—A detailed account, with 11 photographs and figures, of phenomena previously briefly reported (*C. A.* 17, 3131). The rays of a new type are designated γ -rays. Here the α -particle evidently drives particles from 2 widely sepd. atoms in its path. The 2 tracks lie in almost parallel planes; both are highly curved and almost parallel lines, and both have a sharp retrograde motion. The γ -rays are probably due to electron emission; at any rate the particles are very light since the α -particle is undeviated and the tracks are much longer than those of the previously recorded δ -rays.

G. L. CLARK

The β -ray spectrum of UX_1 and its significance. LISE MEITNER. *Z. Physik* 17, 54-66(1923).—The velocities with which β -particles are emitted from UX_1 were measured with the highest attainable precision. They were found to form a "spectrum" consisting of 3 sharp lines and a diffuse band corresponding to velocities of $0.48c$, $0.52c$, and $0.53c$, for the lines, and $0.58c$ for the center of gravity of the band, c being the velocity of light. Only the characteristic Röntgen rays occur in the emitted γ -radiation. The electrons forming the 3 sharp lines originate in the L, M, and N levels and are ejected by the K_α radiation characteristic of the Th isotope UX_1 . The K-radiation is itself excited by the primary β -rays, which form the diffuse band and whose energy

nearly equals that of the K-limit of Th. Thus the entire process from the emission of the primary β -rays from the nucleus of the atom to the liberation of the secondary β -rays from the L, M, and N rings is centered in the atom itself. C. C. KIESS

Methods for standardizing an emanation electrometer. W. BOTHE. *Z. Physik* 16, 266-79(1923).—Three methods are described for standardizing an emanation electrometer: First by means of simple gas pipet, made up of 4 known vols., used to draw off a known fraction of the total which has previously been measured by γ -rays. The readings should be corrected for changes in pressure; the readings change only about $1/4$ as much as the pressure changes. Second, through the decay of Ra emanation. The decompn. const. of emanation was redetd. and as a mean of 4 detns. λ is given as $0.1812 \text{ day}^{-1} \pm 0.1\%$. Third, by employing a standard soln. which has been made up by dissolving a Ra salt previously standardized by γ -ray measurements. M. F.

Note on the formation of negative ions in a gas. R. D. KLEEMAN. *Proc. Phys. Soc.* 1922; *Phys. Rev.* 19, 541-2.—Loeb's (*C. A.* 15, 1249) exptl. results were interpreted to support Thomson's theory rather than that of Wellisch. They can be as well explained by the theory of ion formation and existence proposed by K. (*C. A.* 7, 3904). D. MACRAE

X-ray analysis of luminescent boron nitride. ERICH TIEDE AND H. TOMASCHKE. *Z. Elektrochem.* 29, 303-4(1923).—An address. H. JERMAIN CREIGHTON

Röntgenographic structural phenomena in respect to luminescent calcium tungstate. ERICH TIEDE AND ARTHUR SCHLEEDT. *Z. Elektrochem.* 29, 304-6(1923).—An address. H. JERMAIN CREIGHTON

X-rays and β -rays. M. DE BROGLIE. *Rept. Brit. Assoc. Advancement Sci.* 1922, 352-3.—Mathematical, involving a discussion of the excitation of X-rays by the impact of cathode rays on the anticathode of a tube. C. C. DAVIS

Investigations on X-rays and β -rays by the cloud method. C. T. R. WILSON. *Proc. Roy. Soc. (London)* 104A, 1-24(1923).—The study of several hundred stereoscopic photographs (of which 22 are reproduced) showing the no., distribution, direction of ejection and range of the β -particles emitted from atoms in air exposed to X-rays leads to the following conclusions: (1) The cloud method is able to deal with individual quanta of radiation, in the sense that the track of the electron ejected from the atom which emits the quantum of radiation and that of the electron ejected from the atom which absorbs the radiation can be identified. (2) Two classes of β -ray tracks are produced in air by the primary action of X-radiation of wave length less than 0.5 \AA : those of ejected electrons with initial kinetic energy comparable to the quantum of the incident radiation, and tracks of very short range. The short range electrons are ejected nearly along the direction of the primary X-rays. Their direction and range and value of the min. frequency of the radiation which is required to produce them are in agreement with the suggestion of A. H. Compton, that a single electron may be effective in scattering a quantum of radiation and that in so doing, it receives the whole momentum of the quantum. The short-range tracks are probably related to the phenomena which have led to the postulation of a "J"-radiation. (3) The ordinary long range tracks may be divided into 3 classes according to the direction of the ejection of the electron. The majority have a large forward component comparable with the lateral component; about 20% are ejected almost at right angles to the primary X-ray beam; others have a large backward component. (4) Partial polarization of the primary beams is indicated by the direction of ejection of a no. of the β -particles being in 1 plane—that containing the direction of the cathode rays in the X-ray tube. (5) β -rays in air exposed to X-rays frequently occur in pairs or groups, of which 5 classes are distinguished. The pairs consist of 1 K-electron ejected by the direct action of the primary X-rays, and of one ejected by the combined action of the primary radiation and of the K-radiation from the atom from which the first electron was ejected. G. L. CLARK

The scattering of X- and γ -rays by rings of electrons. The effect of damping of the incident radiation. G. A. SCHOTT. *Proc. Roy. Soc. (London)* 104A, 153-64(1923).—S. examines whether damping of the incident radiation can account for the abnormally small scattering of hard γ -rays by Al, Fe and Pb, which was observed by Ishino, based on the hypothesis that scattering is a phenomenon of the diffraction by electron rings in the atom of undamped simple harmonic wave-trains of high frequency. The result of the mathematical analysis is negative. Damping of an amt. small enough to be consistent with the generation of moderately sharp lines in the X- and γ -ray spectrum diminishes the scattering of long waves, but it increases that of short waves and in each case the change is far too small to explain Ishino's result. On the other hand, very large damping probably diminishes the scattering of all waves but not below the amt. required by the simple pulse theory, while Ishino's values are $1/4$ of that amt. It is

necessary, therefore, to assume that at least some of the rings of Al, Fe and Pb are moving with a speed comparable with that of light ($\beta = (1/2)\sqrt{3} = 0.866$). G. L. CLARK

Problems of X-ray emission. D. L. WENSTER. *Bull. Nat. Research Council* 1, 427-55(1920).—General review of researches upon the following topics: quantum phenomena in the general radiation spectrum, i. e., the short wave length limit governed by $Ve = h\nu$, and the application to the accurate evaluation of h , quantum phenomena in characteristic rays, i. e., the crit. potentials of characteristic X-rays; spectra at different potentials in a single direction and theories of general radiation as impact radiation; spectra in different directions and polarization of X-rays. A bibliography of 73 references is appended. G. L. CLARK

Intensity of emission of X-rays and their reflection from crystals. BERGEN DAVIS. *Bull. Nat. Res. Council* 1, 410-26(1920).—General survey of researches in the fields of total emission of energy from X-ray tubes, intensity of the characteristic (line) spectra of X-rays, the intensity of reflection of X-rays from crystals (cf. *C. A.* 17, 362, 1921 for subsequent work on problems here suggested), and the decrease of electron velocities on penetrating the target. A bibliography of 28 references is appended. G. L. C.

The deviation of X-rays from the surface of a substance and the effect produced by a slit. F. WOLFFERS. *Compt. rend.* 177, 32-4(1923).—Announcement of the discovery of phenomena apparently identical with the total reflection studied by Compton (*C. A.* 17, 2674). G. L. CLARK

The diffraction of X-rays by liquids. W. H. KESOM and J. DE SMEDT. *J. phys. radium* 4, 144-51(1923).—Cf. *C. A.* 16, 4135; 17, 2822. G. L. CLARK

Is there a change of wave length on reflection of X-rays from crystals? G. B. M. JAUNCEY and C. H. ECKART. *Nature* 112, 325-6(1923).—Considering reflection from crystals as a special case of scattering, J. and E. show that, upon the basis of Compton's theory of wave-length change upon scattering from amorphous substances (*C. A.* 17, 2821), $\lambda' - \lambda = \gamma \cos^2 \theta$, where λ' is the apparent wave length from the Bragg law, λ is the apparent wave length when $(\theta_1 + \theta_2)$, the angle of deviation between reflected and incident rays, is observed so that $n\lambda' = 2d \sin (\theta_1 + \theta_2)/2$, and $\gamma = h/mc^2 = 0.024 \text{ \AA}$. Experimentally, however, $\lambda' - \lambda = 0$; hence there is no change in wave length. Differences between λ' and λ , the incident beam wave length are explained by a refractive index. G. L. CLARK

Continuous spectral energy distribution within the X-ray tube. PAUL KIRKPATRICK. *Phys. Rev.* 22, 37-47(1923).—The continuous spectral energy distribution of X-radiation as emitted from a target of a Coolidge tube at right angles to the beam of electrons was detd. from the distribution curve obtained with a rock salt crystal spectrometer and a CH_4I ionization chamber by applying certain corrections for superposed higher orders, for incompleteness of absorption in the ionization chamber, for absorption by glass, air and the Al window and for reflecting power of the NaCl crystal. The final curves show max. at 0.445 and 0.503 \AA . for 71 and 51 kv., resp. Comparison with 3 different theoretical results shows wide divergence from any of them but it is probable that no real agreement is to be expected until more knowledge is obtained relative to the penetration of cathode electrons and the wave-length variation of the mech. equiv. of ionization. W. F. MEGGERS

The vibrational isotope effect in the band spectrum of boron nitride. R. S. MULLIKEN. *Science* 58, 164-6(1923).—Examn. of data on the β system of the band spectrum of BN discloses the presence of two completely analogous sets of bands, one weaker than the other. The relative positions and spacings of the two sets are shown to agree closely, if the stronger set is due to B^{10}N and the weaker to B^{11}N , with what would be predicted from the quantum theory of band spectra, values of the vibrational quantum nos. being first assigned to each band. New data indicate that there is equally good agreement with theory for the α -system of BN. The largest difference so far measured in the position of corresponding bands of the two isotopes is in a red band of the α -system, where corresponding wave lengths of the stronger heads are: B^{10}N , 6368; B^{11}N , 6462 \AA . New bands farther in the red show even greater differences.

R. S. MULLIKEN

The absorption spectra of vegetable dyes of the flavone series. I. YUJI SHIBATA AND KENSHO KIMOTSUKI. *Acta Phytochim.* 1, 91-104(1923).—The vegetable coloring matters of the flavone series show two characteristic absorption curves in the ultra-violet, and since the position of these bands is affected by the no. and orientation of the hydroxyl groups, the ultra-violet absorption spectra serve as a ready means of identifying the different members of the series. The observations are best made in 0.0001 M alc. soln. Flavone itself has the two bands at frequencies 3500 and 4050. The position of the second band is scarcely influenced by hydroxyl groups, but the first is shifted

towards the red by hydroxyl groups in the benzopyrone nucleus, and in the opposite direction by hydroxyl in the side phenyl group. Moreover, the depth of this band increases with the no. of hydroxyl groups, as in the series kaempferol, quercetin, myricetin, contg., resp., one, two, and 3 hydroxyls in the side Ph group. Acetylation neutralizes the influence of the hydroxyl groups, and diacetylchrysin and pentaacetylquercetin have exactly the same absorption spectrum as flavone. In chrysin, apigenin, and luteolin, the head of the first absorption band is near 3500; chrysin is exceptional in that the second band is also shifted considerably towards the red. Galangin, kaempferol, and kaempferide form a closely related group with the first band at 2650. In quercetin, isorhamnetin, and myricetin, this band is also at 2650 but is deeper. The absorption bands of the flavone coloring matters from 17 different plants were examd., and by comparison of the curves obtained with those of the above substances it was possible to det. to what type the unknown substances belonged. Exact correspondence was not obtained, probably on account of impurities in the plant preps. J. C. S.

The absorption of light by several components. N. P. PESKOV. *J. Russ. Phys. Chem. Soc.* 48, 1924-52(1916).—Mixts. of colored substances are examd. spectrophotometrically with a view to ascertaining what mutual influences their components have on each other. Only crystalloids follow Beer's law, separately, or in mixts. The use of dyes, which are mainly colloidal substances, together with crystalloids is valueless for testing Beer's law, and the absorption const. of such mixts. cannot be calcd. by this law. The importance of this observation in connection with the prepn. of quant. light filters for the detn. of wave lengths is pointed out. Mixts. of colloids only in exceptional cases follow Beer's law, but usually vary from it owing to inter-adsorption of the components, and light filters made from mixts. of such substances must therefore in each case be separately calibrated. Thus in a mixt. of colloidal iron and malachite-green, the latter substance distributes itself between the water and the colloidal hydrated $\text{Fe}(\text{OH})_3$ in a const. ratio, depending on the concns. of the two components. The value of spectrophotometric analysis for the investigation of the detailed processes of a reaction and the identification of intermediate products is emphasized. J. C. S.

Joining the infra-red and electric wave spectra. E. F. NICHOLS AND J. D. TEAR. *Proc. Nat. Acad. Sci.* 9, 211-4(1923).—An improved app. consisting of a modified and highly sensitive Nichols radiometer, a Hertzian oscillator, and interferometer, and a secondary receiver which checks the performance of the oscillator, has made it possible to produce and measure short elec. waves from the shortest hitherto measured to a length of 0.220 mm. The longest heat waves measured by Ruhens and Von Baeyer were 0.320 mm. and their results were verified by the new app. and method. Thus the complete spectrum is bridged, ranging from the longest elec. waves to the γ -rays of Ra, with the exception of 3.3 octaves between the longest X-rays and the shortest ultra-violet rays. C. C. KIESS

Direct-reading photoelectric measurement of spectral transmission. K. S. GIBSON. *J. Optical Soc. Am.* 7, 693-704(1923).—Combining the Brodhun variable sector with the method of equal deflections has resulted in a new *direct-reading* method of measuring spectral transmissions. It eliminates errors inherent in other methods, has high precision, and requires no computing. The *direct-reading* method used with the thermopile instead of the photo-elec. cell may be used satisfactorily in the red and near infra-red. By means of the photoelec. *direct-reading* method and the thermoelec. ratio-of-deflections method, transmissions may be reliably measured throughout the visible spectrum. C. C. KIESS

A spectrographic study of ultra-violet fluorescence excited by X-rays. J. O. PERRINE. *Phys. Rev.* 22, 48-57(1923); cf. C. A. 17, 3134. W. F. MEGGERS

Theory of band spectra. H. A. KRAMERS AND W. PAULI, JR. *Z. Physik* 13, 351-67(1923).—The theory discussed differs from others in that heretofore the theory of band spectra in general used only models of 2-atom mols. in which either no resultant electron impulse-moment existed or this moment had the direction of the line joining the nuclei so that the mol. acted as a rigid symmetrical top, while the present treatment assumes that the electron impulse-moment makes a given angle with the joining line. A solu. of the problem in mechanics is based on another paper by K. (C. A. 17, 3127) dealing with the quantizing of rotating mols. Then it is shown that the observations on infra-red spectra of halogen hydrides can be brought into agreement with the theory and that the noble gases and similarly constructed negative halogen ions possess a resultant electron impulse-moment of $\hbar/2\pi$ as apparently required by the Bohr theory of the periodic system. The assumption that the mol. may be regarded as a rigid body and that the direction of the electron impulse-moment rotates rigidly with the mol. is tested on questions concerning the fine structure of bands and

their Zeeman effect. It is concluded that there are many cases where the assumption of rigidity is not valid and the mol. is to be regarded rather as a rotating positive mol. ion in whose field of elec. force the radiating electron moves. W. F. MCGREGG.

The absorption of near infra-red radiation by carbon dioxide. JUNZO OKUBO, *Sci. Repts. Tôhoku Imp. Univ.* 12, 39-43 (1923).—By employing a Hilger infra-red spectrometer with a Nernst glower as a source and a sensitive Rubens thermopile as a receiver of spectral energy transmitted by CO_2 in an absorption tube of 20 cm. length, the 2 or 3 strong absorption bands previously recognized in the vicinity of 22.7μ are shown to be more complex. Three strong maxima of absorption occur at 22.61μ , 2.71μ , and 2.77μ , resp. There are many weaker bands at intervals of about 0.06μ and 0.04μ , and the wave lengths of 18 are given in the interval 2.20 to 3.02μ . W. F. MCGREGG.

The distribution of intensity in the broadened Balmer lines of hydrogen. E. O. HULBERT. *Phys. Rev.* 22, 24-36 (1923); cf. *C. A.* 16, 3261. Under usual excitation by a transformer or induction coil the lines of the Balmer series of H at low pressure are sharply defined. When the gas pressure is increased to several hundred mm. Hg and when condensed discharges are employed, the lines increase in intensity and width until almost unrecognizable. This broadening has received unusual attention because of its large magnitude and because of the importance of the H atom in theories of at. structure. The present investigation deals with the nature and the probable cause of the broadening. The intensity distribution in H α , H β , and H γ was detd. at various pressures (48 to 250 mm.) by photographing the spectra through a neutral wedge filled with an aq. soln. of a black dye. In each case the broadening was sym., amounting to about 60 Å. for each line at 250 mm. but the curves gave evidences of structure characteristic of each line. The effect of a quenched gap in series with the tube was to increase the broadening, while inductance decreased it. In mixts. with He or N $_2$ the broadening was the same as in H alone at the same total pressure. A theory of broadening based upon the Stark effect of the elec. fields of the ionized atoms or the radiating atoms is given mathematical formulation by assuming a probability law for the distribution of the atoms and ions, an inverse-square law for the field strength, and introducing Sommerfeld's quantum expression for the Stark displacement. Comparison with expt. shows agreement as to the general form of the intensity distribution. The great broadening produced by the condensed discharge is then due to the momentary high current density and corresponding large proportion of ionized atoms. W. F. MCGREGG.

Ionization of helium and excitation of the spectra by slow-moving electrons. G. DEJARDIN. *J. Phys. Radium* 4, 121-8 (1923).—The crit. velocities of electrons in He, detd. by different experimenters, correspond to 20.4, 21.2, and 25.2 v. The first, according to Franck and Kuipping, is the min. velocity which an electron must acquire to make the He atom pass from its normal state, in which the two electron orbits are crossed, to a coplanar configuration. If this be true the first crit. potential of He is not a resonance potential; it represents the energy involved in an allotropic transformation of the gas. The second crit. velocity corresponds to the emission of resonance radiation and the third to ionization of the normal atom. In addn. increased ionization has been observed for 55 to 80 v., which is believed to represent double ionization of the normal He atom, giving rise to the spark spectrum of He. With a classical type of 3-electrode tube expts. were made to seek the origin of ionization in pure or in impure He traversed by electrons whose velocities are less than the crit. velocity of ionization and to det. precisely the conditions of spark spectrum excitation. Elec. measurements and spectrographic observations were made simultaneously. It was found that ionization of He at several tenths of a mm. Hg commences at 25.2 v., and simultaneous emission of two sets of spectral series (those of so-called ortho He and of par He) takes place. When the He gas pressure reaches several mm. Hg appreciable ionization is produced at 20.4 v. by successive impacts and at lower pressures it is possible to detect some ionization below 25 v. if the electron current is very intense. In the latter case the ionization is due to the photoelec. effect of radiation excited at 21.2 v. upon the metastable atoms which are formed at 20.4 v. Peculiar effects are observed when a trace of Hg vapor is present. The band spectrum of He cannot be observed unless the gas pressure exceeds 3 mm. It is probable that the min. electron velocity for excitation of the band spectrum corresponds also to 20.4 v. At pressures below 3 mm. the spark lines 4686, 3203 and 2733 Å. appear strongly at 50 v. They are readily observed at 51 v. when the pressure of the gas is 4 to 8 mm. but cannot be seen for pressures of 10 mm., since the no. of electrons which can acquire the min. velocity required for double ionization is probably too small at the higher pressure. W. F. MCGREGG.

Series in the arc spectrum of molybdenum. C. C. KRESS. *Bur. Standards, Sci. Papers* 19, 113-29 (1923).—Many of the strong lines of the arc spectrum of Mo

have been found to be members of series. These are of several types. Narrow triplets characterized by the wave-no. differences 121.5 and 87.0 have been arranged into the series $1S - mP_1$, $2P - mS$, and $2P_1 - mD_1$. Widely sepd. triplets, between which the wave-no. differences 448.5 and 257.5 exist, form the series $1s - mp_1$, $2p_1 - ms$, and $2p_1 - md_1$. Parallel to these wide triplet series are other series $1s - (mp_1 + k_1)$, $(2p_1 - k_1) - ms$, and $(2p_1 - k_1) - md_1$, of which the wave-no. seps. 379.9 and 233.4 are characteristic. The limits of these series have been calcd. with formulas of the Ritz type and with the aid of the inter-series combination lines $1s - 2P_1$, $1s - 2P_1$, $1S - 2p_1$, and $1S - 2p_1$. From the known values of $1s$ and $2p_1$ it follows that the resonance and ionization potentials of Mo are 3.25 and 7.35 v., resp. In addn. to the triplets there occur in the spectrum of Mo groups of 9, 10, and 13 lines known as multiplets, which arise from the combinations of the various three-fold and five-fold levels which exist beyond the $1s$ level of the atom.

C. C. KIESS

The absorption and anomalous rotation dispersion of camphorquinone. NINA VEDRNERVA. *Ann. Physik* 72, 122-40(1923).—Measurements of the rotation, ellipticity and absorption of camphorquinone were made in the region of its absorption bands and the results are discussed from the standpoint of the Drude theory. The activity coeffs. are calcd. Methods are given for the measurement of phase difference and dichroism.

F. O. ANDEREGG

The exciting absorption and destruction of phosphors. E. RUPP. *Ann. Physik* 72, 81-121(1923); cf. Lenard *C. A.* 11, 1079.—The distribution of the amt. of light, of the exciting absorption and of the destruction of centers of phosphorescence with reference to the wave length of light has been studied and a special method has been used for O-phosphors. Cathode rays excite the max. amt. of destruction-free light for centers of long life. The formation, spectral regions and abs. value of the amt. of light are compared for different phosphors. For the exciting absorption a normal and a selective photoelec. effect are proved and quant. studied. The phosphor centers were shown to have both space and time variations in their oscillation periods. The short wave destruction is proved to be a photoelec. action on the genus atom of the phosphorescence. The threshold value of this action is established and compared with other expts. on work of sepn. and min. energy of expulsion. With a Zn-Cu phosphor the original connection between destruction and change in dielec. const. during illumination is proved. As a general rule the sepn. of a photoelec. electron in a medium of dielec. const. ϵ requires less energy in the ratio $\epsilon^{1/2}:1$ than in ether.

F. O. ANDEREGG

Fluorescence and photochemistry. R. LEVAILLANT. *Compt. rend.* 177, 398-401 (1923).—Sols. of many fluorescent substances like the fluoresceins at a concn. of 1/5000 in polyalcohols or certain org. acids are bleached *in vacuo* by radiation near the ultraviolet, becoming hydrogenated. Many give the same reaction when heated, supporting Perrin's theory that fluorescence renders the mol. chemically active. The reaction did not occur when the concn. was increased or when non-fluorescent substances were used. Heating in air restored the color.

G. R. FONDA

The superposition of electromotive forces in cells of fluorescent liquids. A. GRUMBACH. *Compt. rend.* 177, 395-8(1923).—A dil. soln. of Na_2CO_3 contg. a fluorescent salt gives rise to a + e. m. f. if one of the Pt electrodes is illuminated by light from a Hg arc, but further diln. changes it to —. When only the soln. between the electrodes is illuminated, the e. m. f. is —.

G. R. FONDA

Chemiluminescence. H. KAUTSKY AND H. ZOCHER. *Z. Elektrochem.* 29, 308-12(1923).—An address.

H. JERMAIN CREIGHTON

The question of the proportionality between luminous intensity and photoelectric current in alkali metal cells containing a rare gas. H. V. HALBAN AND L. EBERT. *Z. Physik* 14, 182-90(1923).—Expts. with 5 different cells, with monochromatic light of 450 μ , gave the same ratio for photoelec. current as for light intensity at voltages below that at which a glow forms, in accordance with previous work of others. As the arrangement of app. was similar to that of Steinke (*C. A.* 17, 2822) the results demonstrate that his cells were abnormal in showing wide deviations from proportionality and make evident the necessity for careful selection of cells for use in photometry.

G. R. FONDA

Betafite (DUMAS) 8. Presence of carnotite in the Congo (SCHÖPP, RICHET) 8. Absorption spectra and chemical constitution of organic compounds (BALY, *et al.*) 10. Formulating the periodic system of the elements (PANETH) 2.

BRILLOUIN, LÉON: La théorie des quanta et l'atome de Bohr. Paris: Albert Blanchard. 184 pp.

PRINGSHEIM, PETER: *Fluoreszenz und Phosphoreszenz im Lichte der neueren Atomtheorie*. 2nd ed. Berlin: Julius Springer. 228 pp.

4—ELECTROCHEMISTRY

COLIN G. FINK

Electric furnace demonstrates flexibility in steel foundry. J. L. McK. YARDLEY. *Elec. World* 82, 479-84(1923).—A description of a 6-ton Ludlum furnace installation at the Trafford foundry of the Westinghouse Co. The metal is handled by crane ladles and the furnace is elevated to a height sufficient to obviate the necessity for a deep ladle pit. Advantages of this arrangement are: (1) it permits mounting the tilting motors and machinery where danger is less due to hot metal or water; (2) it keeps the crew away from the molders; and (3) it cuts the time in all operations of ladle and makes easier the slag disposal. Disadvantages are: (1) requirement of a more expensive structure; (2) all materials must be carried to the platform. The furnace, the arrangement of conductors between furnace and transformer, the automatic regulators, meters, and furnace-control panel are illus. Two easily eliminated defects of the new furnace are: the roof does not last as well as the regular circular type roof and the electrode masts lack rigidity against side whip. Despite these faults, the furnace is a com. success. Uses of acid and basic linings and some operating results are listed. W. H. BOYNTON

Producing synthetic gray iron in the electric furnace. E. L. WILLSON. *Elec. World* 82, 431-3(1923).—An account of tests to det. (1) the com. possibilities for a central power station to produce synthetic pig Fe using off-peak power at a price to compete with blast furnace Fe and (2) the cost and quality of synthetic gray Fe made direct into castings as compared with cupola Fe castings. Both acid and basic melting were tested. Basic melting allowed greater range in the selection of raw materials and permitted more ready absorption of C. A central station must be favorably located with respect to a supply of scrap and a market for pig Fe in order profitably to use off-peak power in the production of synthetic pig Fe. Such castings may be as low or lower in cost than better grades of cupola Fe, and have phys. strength and toughness far in excess of the best cupola Fe. LOUIS JORDAN

Manufacture of cast iron in the electric furnace. L. LYCHE. *Stahl u. Eisen* 43, 110-6(1923).—Expts. were carried out over a period of 4½ months in a new type of elec. pig Fe furnace with two shafts. The production of cast Fe in such a furnace demands that the 3 following conditions be fulfilled, viz., high temp., excess of fuel, and long working period. In general the simultaneous attainment of these 3 conditions is not easy, so that the successful production of cast iron in the elec. furnace is difficult. Results are given comparing the type of furnace used with other types of elec. furnaces; and the heat balance of the furnace for a working period is discussed. J. C. S. I.

Electric production of pig-iron. ASSAR GROENWALL. *Teknisk Ukeblad* 41, 164(1923).—A reply to Lorentzen (cf. C. A. 17, 2835). G. prefers his own furnace type, the Elektrometal-type, to the Tinnfoss-type even for mfg. high-C pig-iron with coke as a fuel. In this case he uses lower shafts, only 2-3 m. even in large furnaces. The roof electrodes are protected against burning by water-cooled steel rings around the holes where the electrodes pass through the roof. Other details are given. C. H. A. S.

Advantages of basic electric furnace iron for castings to resist abrasion. L. J. HARTON. *Eng. Min. J. Press* 115, 628-30(1923).—Basic elec. furnace white Fe castings (synthetic Fe) are better than acid elec. furnace Fe and far superior to cupola white Fe for grinding and abrasive work. The superiority of the basic elec. furnace iron castings is due to the fact that they are free of blow holes, internal shrinks, or gas pockets; free of dirt or other non-metallic inclusions; that they do not show segregation of S or P; that the Fe will run clean and be of correct chem. compn. Comparative tests of crusher jaws and rolls have been distinctly in favor of the elec. Fe. LOUIS JORDAN

Molten additions to steel. FRANK HODSON. *Elec. World* 82, 441-2(1923).—An elec. furnace with bottom electrode will ensure at a low operating cost a supply of liquid ferro-Mn for addns. to open-hearth and converter steels. With such a melting equipment as much as 25% of the charge may be Mn ore. The bottom electrode is necessary to prevent segregation of Mn at the bottom of the bath. LOUIS JORDAN

A heat balance for an electric steel furnace of the Röchling-Rodenhauser type. O. VON KEIL AND W. ROHLAND. *Stahl u. Eisen* 43, 1095-1102(1923).—The furnace is a 2-phase induction type, using a c. of 150 to 200 amp. at 6000 v. and 16.6 cycle. The furnace is of a two-charge type and has a capacity of 8 to 12 tons. The radiation and conduction losses were thoroughly investigated by placing thermocouples at various

points in the lining and shell of the furnace as shown by a sketch given, and the temps. carefully taken. Radiation and conduction losses were calcd. according to the formulas of J. W. Richards. The cool air was measured by a Pitot tube and the temp. by 4 Hg thermometers. The atm. in the furnaces was controlled by the analyses of the gas from time to time. The melt was made in a Siemens-Martin furnace and then poured into the elec. furnace. The times and conditions were noted at different periods and tabulated in tables with the wt. and analysis of slags, steel, charged material and gas, together with the various temps. One characteristic noted from the tables was that, as the FeO content of the slag increased the MnO likewise followed and *vice versa*. The oxidation of the ferro-Si, consumption of C by the bath, rephosphorization due to slag and action of Mn and S are discussed for the different periods. The heat efficiency of the furnace was about 62%. By various changes suggested this could be increased. With a lessened Cu loss in transformation it is said that an efficiency of 66.5% could be made, and with these added precautions and changes the cost per ton of steel would be decreased by 12.5%.

W. A. MUELLER

Lining acid electric furnaces. J. M. QUINN. *Iron Age* 111, 1101-2(1923).—Materials used for acid elec. furnace linings are crushed ganister rock (through $\frac{1}{4}$ -in. mesh, 50% $\frac{3}{4}$ -in. and finer) contg. about 98% SiO₂, used where high temps. are essential; ground ganister ($\frac{1}{4}$ -in. mesh with a large proportion of fines) contg. about 96% SiO₂, used where ordinary steel pouring temps. are required; furnace bottom sand contg. about 94% SiO₂, or as a substitute new silica molding sand mixed with a small amt. of fire clay; and silica brick. The best furnace lining is silica brick with sand bottom burned in layer by layer. A cheaper method of lining, and nearly as satisfactory, is to use rammed in crushed ganister rock, sectional wooden forms being employed to shape the lining. Ground ganister mixed with old silica brick broken to $\frac{3}{4}$ -in. is used for lining in the same manner as crushed ganister rock. Door jams and arches should, however, be made of brick in any rammed lining. Roofs are usually of silica brick. Well designed cubical blocks spall less readily in roofs than standard shape bricks. A layer of poor heat conductor next to the inside furnace wall is often specified. This frequently causes short life of refractories. Furnaces without this heat insulation often result in better operating conditions, lower refractory cost, and no apparent increase in kw. hr. used per ton of steel. Heat insulation should never be used when refractories are to be used at their limiting temp. Cf. following abstr.

LOUIS JORDAN

Acid electric steel furnace operation. J. M. QUINN. *Iron Age* 111, 1177-9(1923); cf. preceding abstr.—The controlling factor in the operation of the acid elec. furnace seems to be the quantity of iron oxide present when the heat is melted whether it is introduced as rust with the scrap, or results from oxidation due to air leaks or from ore adds. This oxide reacting with SiO₂ directly controls the slag vol. Correct proportioning of the scrap charge and uniform melting practice will give a bath which is deoxidized in 10 to 15 min. after melting. If C is high in the first test of metal, ore or scrap is added. Such decarburization gives a large vol. of black or oxidizing slag. This is removed and a fresh slag made with silica sand. Adds. of coal or coke may be made to reduce Fe and Mn oxides in the slag. During the low temp. period of the melting down of the charge oxidation of Si takes place in preference to oxidation of C. At higher temp. this condition is reversed—C reduces SiO₂ and the nascent Si deoxidizes the bath. This reaction is the essential point that accounts for the difference between acid and basic steel. Oxides in the slag mean oxides in the steel. As the slag gets lighter in color through the lowering of its basic oxides, oxides in the metal are also lowered. Judicious adds. of burnt CaO aid in reducing basic oxides since the CaO unites with SiO₂, displacing FeO which is then reduced either by the C in the bath or the C thrown on the slag. Methods of charging scrap and the use of deoxidizers in the ladle are also described.

LOUIS JORDAN

Constant-temperature regulator for electric furnaces. JEAN SOLARI. *Bull. soc. chim.* 33, 1000-4(1923).—A device is described for maintaining const. within $\pm 5^\circ$ (at 575°) the temp. of a resistance furnace. The regulator is a differential air thermometer actuating a Hg column which connects or cuts out added resistance in series with the main furnace. An auxiliary furnace in series with the furnace to be regulated contains the hot bulb of the differential thermometer. The main furnace is thus entirely free of obstructions. The auxiliary furnace has little thermal lag, thus causing the regulator to respond promptly to variations in the furnace current.

LOUIS JORDAN

The anode effect. KURT ARNDT AND HANS PROBST. *Z. Elektrochem.* 29, 323-34 (1923).—The anode effect, or disturbance which takes place at the anode during the electrolysis of molten salts, has been studied with CaCl₂, SrCl₂, BaCl₂, PbCl₂, NaCl, KCl, NaF, Na₂AlF₆, NaOH and KOH. Graphite and 2 kinds of C electrodes were used.

With each of the salts the crit. c. d. (i. e., the c. d. at which the phenomenon is manifested) was detd. The values obtained for the crit. c. d. varied between 20 (with KOH and NaOH) and 1 amp./sq. cm. (with BaCl₂). The presence of impurities raises the crit. c. d. With some of the salts the crit. c. d. increased with the porosity of the electrodes employed; with others it decreased, while with NaCl it appeared independent of the porosity of the electrodes. Various factors which influence the anode effect are discussed.

H. JERMAIN CREIGHTON

Advantages of high frequency induction furnace. R. DUFOUR. *J. four électrique* 32, 47-8(1923).—The high frequency induction furnace on account of its ability to produce very high and easily controlled temps., either in vacuum or any desired atm., has enabled the undertaking of research problems which hitherto have been hardly possible. (Cf. Northrup, *C. A.* 15, 1255).

LOUIS JORDAN

The electrolytic methods of hydrogen gas production. J. B. C. KERSHAW. *Engineer* 134, 315-8(1922).—The development of the industry is reviewed. As familiar types the Lane-Messerschmidt, the International Oxygen Co., the Levin and the Knowles cells are illustrated and described.

D. B. DILL

Metallized electrodes of porous porcelain and the simplest form of the acid alkali cell. K. A. HOFMANN. *Ber.* 56B, 1456-63(1923).—Cells have been constructed in which porous porcelain tubes metallized with Pt, Pd, or Ir serve both as gas electrode and diaphragm. If the metallized porcelain tube is designated as *ptr*, *pdr*, or *irr*, the 2 N NaOH as *l*, the 2 N H₂SO₄ as *s*, the platinized Pt electrode by *pt*, and the tubes satd. with acid or alkali by *ptrs* and *ptrl*, then the cells' e. m. f.s. are as follows: H₂-*ptrs*-*l*-*pt*-H₂, with acid satd. tube dipped in alkali, 0.72 v.; H₂-*ptrl*-*s*-*pt*-H₂, with alkali satd. tube dipped in acid, 0.72 v.; O₂-*ptrs*-*l*-*pt*-H₂, 1.58 v.; O₂-*pdr*-*l*-*pt*-H₂, 1.55 v.; O₂-*irr*-*l*-*pt*-H₂, —1.74 v.; H₂-*ptrl*-*s*-*pt*-O₂, 1.75 v.; H₂-*pdr*-*s*-*pt*-O₂, 1.705 v.; H₂-*irr*-*s*-*pt*-O₂, 1.79 v.; and O₂-*irr*-*s*-*pt*-H₂, 0.32 v.

D. MACRAE

Bleaching liquor produced from salt and water by means of low voltage cells. ANON. *Paper Ind.* 5, 779-80(1923).

A. PAINNEAU-COUTURE

Intermittent current electrolysis. 1. The influence of intermittent current on overvoltage. SAMUEL GLASSTONE. *J. Chem. Soc.* 123, 1745-50(1923).—An electrolytic cell was set up with a given metal as cathode and a d. c. of 0.15 amp. passed for 10 min. The voltage at different current densities was measured at intervals of one min. by the Poggendorf compensation method with a capillary electrometer. The d. c. was then replaced immediately by an intermittent current, and the potentials were again measured with the current flowing. The intermittent current was unidirectional and supplied by a Tungsar rectifier. The overvoltage values are consistently lower in the case of the intermittent current. The difference between the intermittent and the direct current is greater the greater the c. d. The difference between the two values is thought to be due to the lowering of the potential caused by the alternating induced current set up by the repeated make and break of the polarizing current in the intermittent current.

C. R. PARK

The single potential of arsenic and its power to replace other metals in solutions. LOUIS KAHLBERG AND J. V. STEINLE. *Trans. Am. Electrochem. Soc.* 44, (preprint).—Detns. of the single potential of As in several different electrolytes confirm those previously found (0.55 v. for the chloride). Electrodes were prepd. in different ways and the best results were obtained with solid As electrodes. Electroplating of As on other metals gave unreliable results. Metallic As replaces metals such as Ag, Cu and Hg from their compds., the reaction being represented as follows: $6MX + 2As + 3H_2O = 6M + 6HX + As_2O_3$, where *M* = monovalent metal and *X* = a monovalent acid radical. As was replaced from its compds. by other metals. The power of a metal to replace another is a highly specific property depending upon the individual nature of the metals and upon the liquids used in the expts. The order of sequence in the voltaic series is often reversed.

W. H. BOYNTON

Chromium plating. W. PFANHAUSER. *Chem.-Ztg.* 47, 581(1923).—A notice concerning an electroplating process for Cr developed by Liebreich and placed on the market by Elektro-Chrom G. m. b. H., Berlin, and Langheim-Pfauhauser Werken A. G., Leipzig-Sellerhausen. By it Cr is obtained with either a polished or mat surface, resembling Pt in appearance, and very resistant to the action of the atm., most chemicals, high heat and abrasion. Almost as hard as corundum and with a high m. p., Cr so prepd. finds many uses in making furnaces, ignition app. for internal combustion engines, elec. devices, etc. It is claimed that the initial cost of a plant is comparable to that of one for Ni plating, and that the operating costs are low.

W. C. EBAUGH

Current distribution and throwing power in electrodeposition. H. E. HARRING AND WM. BLUM. *Trans. Am. Electrochem. Soc.* 43, 365-97(1923).—"Throwing power"

is defined as the deviation (in %) of metal distribution ratio from the primary current distribution ratio. It is dependent upon: the rate of change of cathode potential with c. d.; the resistivity of the soln., and the cathode efficiency at different c. ds. A formula is derived and the detg. factors are found to be: the difference in the single cathode potentials at the two points concerned during current passage, the c. d. obtained upon the least accessible part, the resistivity of the soln., and the const. K which is fixed by the equipment and arrangement used. Exptl. measurements were obtained by using a hard rubber box, with cross-section of 10×10 cm., length 60 cm. and having narrow slots in the sides and bottom for holding the anode and the cathodes in any desired positions. The anode consists of gauze of the metal to be tested. The app. is illusd. and curves show the relation between the cathode potential and the c. d. for various CuSO_4 solns. The effects of c. d., heat and agitation, Cu concn., acidity, and addn. reagents are tabulated, also some results with $\text{Cu}_2(\text{CN})_2$ solns. A statement of the throwing power in any soln. is meaningless unless the value of K and of the c. d. upon at least one of the two parts considered is also specified. $T = 100x \left(\frac{e_f - e_a}{E_f} \right)$, where T =

throwing power, e_f = cathode single potential at f , e_a = cathode single potential at a and E_f = potential through soln. only, from anode to f .

W. H. BOYNTON

Primary cells with atmospheric oxygen depolarization. AL. NASARISCHWILY. *Z. Elektrochem.* 29, 320-3 (1923).—Primary batteries with direct and indirect atm. O_2 depolarization are described. With an air-C electrode the effect amounts to but 0.03 amp. per d. cm.² of effective surface, while with a CuO electrode it amounts to 1.2 amp. under the same conditions.

H. JERMAIN CREIGHTON

Quartz glass ozonizers. HERBERT FISCHER. *Z. Elektrochem.* 29, 318-20 (1923).—Under similar standard conditions the O_3 concn. in the quartz ozonizer is considerably less than in a glass ozonizer. The low concn. of O_3 cannot be ascribed to the transparency of quartz to short-wave radiation, for such radiation has not been detected on the outside of the quartz glass ozonizer. Under similar exptl. conditions quartz and glass ozonizers of the same dimensions yield the same O_3 concn. with a Tesla current. Accordingly, the elec. losses in quartz glass have an appreciable influence on the O_3 concn. From this it is concluded that these losses depend largely on the applied frequency.

H. JERMAIN CREIGHTON

Recent progress in the production of ozone with high tension discharges. F. E. HARTMAN. *Trans. Am. Electrochem. Soc.* 44 (preprint).—The production of O_3 by the silent discharge is described. The energy density of an ozonizer is a straight line function of the cycles and the yield of O_3 is a straight line function of the energy production, at atm. pressure. Ozonizing at high gas pressures induces a better cooling of the electrodes, making high concns. with high energy densities possible. First costs mitigate against the extensive use of ozonizers. An app. for detg. the energy yield of O_3 is illus.

W. H. BOYNTON

The formation of gaseous ions in the oxidation of nitric oxide. A. K. BREWER AND FARRINGTON DANIELS. *Trans. Am. Electrochem. Soc.* 44 (preprint).—Exptl. data show that ions can be formed when NO is oxidized in an elec. field. When using a special form of chamber and oxidizing 50 cc. of NO per min. in a field of 453 v. per cm. a current of the order of 10^{-14} amp. is developed. This corresponds to about 1 ion for every million molecules reacting. No evidence of a saturation current could be detected. Several hypotheses are given to explain the results.

W. H. BOYNTON

Two photographic methods of studying high-voltage discharges. K. B. McEACHRON. *J. Am. Inst. Elec. Eng.* 42, 1045-50 (1923).—A description of 2 methods of drawing out the a. c. corona discharge along a time axis. The first method consists in photographing, with the usual camera, the discharge from a needle point revolved by the alternator which is the source of supply for the high-voltage transformer. The needle is revolved inside a porcelain tube whose outside surface is made conducting and grounded. The second method makes use of a special camera using mirrors revolved synchronously by the alternator itself. This camera is equipped with a shutter so arranged that photographs of sparks may be taken using one sweep of one of the mirrors. Photographs showing the different discharges under varying conditions are included.

C. G. F.

Electricity in flames. H. A. WILSON. *Trans. Am. Electrochem. Soc.* 44 (advance copy).—A review of the history and present status of the subject with a classified bibliography. All alkali salts give ions having nearly the same mobilities, that of neg. ions being very much greater. The ionizations of alkali metals in flames are approx. in accordance with Saha's theory.

W. E. RUDER

Carbon tetrachloride extinguishers on electric fires. S. H. KATZ, E. J. GLRIM

AND J. J. BLOOMFIELD. Bur. of Mines, *Repts. of Investigations* No. 2499, 16 pp. (1923).—Exptl. results are given on the extent and the nature of the hazards to fire-lighters from gases and smoke produced by the application of CCl_4 extinguishers to elec. arcs, burning insulation or fire occurring in elec. app. and machinery. Also the toxic effects of these gases have been tested. COCl_2 , HCl , and Cl are liberated in dangerous concns. from the application of a 1-quart CCl_4 extinguisher and should not be applied to a fire in a confined space from which escape is impossible and from which the gases would not be removed by ventilation. Except under this condition this type of extinguisher is the most satisfactory known. W. H. BOYNTON

Porous metals [for electrodes] (Brit. pat. 194,355) 9.

Galvanic batteries. H. BARDT. Brit. 194,341, Oct. 10, 1921. The electrolyte of a storage battery consists of a soln. of the perchlorate of the metal forming the active material, the support for the active material consisting of a metal or alloy such as ferro-Si, which is inert with respect to the electrolyte. The electrolyte consists of a soln. of Pb perchlorate of a concn. corresponding to 40% of metallic Pb. The positive electrode of ferro-Si is placed horizontally at the bottom of the container and carries a quantity of PbO corresponding to the metal content of the electrolyte. The negative electrode consists of ferro-Si or other metal or alloy. In another example, the electrolyte consists of a soln. of Cu perchlorate of a concn. corresponding to 13% of metallic Cu, the positive electrode carrying a corresponding quantity of CuO .

Galvanic batteries. H. D. NYBERG. Brit. 195,580, June 12, 1922. A cell is provided with an electrolyte consisting of a soln. of the hydroxide of one or more alkali metals, or of NH_4 , the concn. being such that it remains practically unaltered during the working of the cell. This value of the concn. is less than or nearly equal to the concn. at which the soln. has a max. capacity of dissolving the hydroxide of the metal forming the positive electrode, such as Zn. Salts, such as NaCl , capable of pptg. the hydroxide of the metal of the positive electrode may also be added to the electrolyte. In an example, C and Zn electrodes are immersed in a soln. of 90 g. of NaOH dissolved in 1 l. of H_2O . Other examples are given.

Galvanic batteries. H. LEITNER. Brit. 195,477, Jan. 21, 1922. In order to assist the electrolytic reactions in storage batteries employing as active material pastes consisting of oxides of Pb with glycerol, treacle, molasses, tar, etc., oxidizing or conducting substances are added to the pastes. In an example MnO_2 is added to the active material consisting of PbO and glycerol dild. with H_2O to form a paste. The MnO_2 is ultimately dissolved out of the active material leaving it in a porous condition. PbO_2 made electrolytically may also be added to the paste, particularly for positive electrodes, and powd. electrolytic spongy Pb may be added to the paste, particularly for negative electrodes. The PbO_2 and spongy Pb may be obtained from old accumulators. Cf. 5104, 1881.

Electrode for the production of ozone. CHEMISCHE FABRIK BRUGG A.-G. Ger. 299,248, June 29, 1917. The electrode is made up of a metal coating sprayed upon a non-conductor such as a glass tube.

Protecting electrodes passing through fire-brick walls. E. A. A. GROENWALL. Swed. 53,757, Feb. 14, 1923. The electrodes are cooled at those sections that pass through the wall. Extra cooling segments are placed on the wall outside the layer of bricks immediately surrounding the electrodes.

Electrolysis. R. RODRIAN. Brit. 194,314, March 5, 1923. A charge of metaliferous material is smelted above a body of molten metal, such as Pb or Pb alloy, and is then electrolyzed with the molten metal as cathode. A suitable construction is specified. Cf. C. A. 16,3625.

Manganese or lead peroxide. H. BARDT. Brit. 194,340, Oct. 10, 1921. A soln. of perchlorate of Mn or of Pb or a mixt. of both contg. a great excess of free HClO_4 is electrolyzed, an anode of a conducting substance inert to HClO_4 being used; Mn or Pb peroxide or a mixt. of both is deposited on the anode which is then used as an electrode in other electrolytic processes. The soln. may be prepd. by dissolving 90 g. of MnCO_3 or 150 g. of PbO in 1 l. of 20% HClO_4 . The anode may be of ferro-Si or magnetic oxide of iron and the cathode of Cu or Pb plates. A current density of 0.3 to 0.5 amps. per sq. decimeter of anode is used at first and after a compact uniform and thin layer is deposited it is raised to 2.5 to 3 amps. to produce a honeycombed structure of the deposit.

Electrolytic beryllium. H. GOLDSCHMIDT and A. SROCK. Brit. 192,970, April 19, 1922. Be is obtained in a pure compact form by electrolysis of a fused double fluoride of Be and an alkali metal in the presence of an alk. earth fluoride at a temp. ap-

proaching the m. p. of Be, *e. g.*, 1280° and upwards. In an example double fluoride of Be and Na is fused in a graphite crucible and gradually increasing quantities of double fluoride of Ba and Be are added, electrolysis being commenced when the bath reaches 1200–1300°. Either of the double salts may be added to replace the Be sepd. A hollow water-cooled iron rod may be used as cathode.

Electrolytic iron. F. A. EUSIS. Brit. 194,639, Dec. 22, 1921. In order to produce an electrolyte for the deposition of the metal, Fe_2O_3 , which may be in the form of a natural or roasted ore, is dissolved by a weakly acid soln. of a ferrous salt, such as the chloride or sulfate; this soln. is said to be an efficient solvent for Fe_2O_3 . A suitable app. is specified. Cf. C. A. 17, 243.

Electrolytic iron hydroxide. WATERLOO CHEMICAL WORKS, LTD. Brit. 195,077, March 14, 1923. A soln. contg. a neutral salt of an alkali metal such as NaCl, and also a small quantity of H_2SO_4 or other free acid, or of an Fe salt such as copperas is electrolyzed with an Fe anode. The electrolyte is supplied continuously; $\text{Fe}(\text{OH})_2$ rises to the surface and flows away over a launder to a filter press. The hydroxide is converted to the ferric state by drying and roasting. The filtrate is returned with fresh electrolyte to the cell. The anode may be of tin-plate, galvanized Fe or black Fe scrap either loose or pressed into blocks. The cathode may be of sheet Fe or Pb.

Fluorides. B. WIESMANN. Ger. 302,117, Nov. 26, 1917. Fluorspar is heated with alkali sulfate, especially K_2SO_4 , and C. Enough electrically conducting C is used above the amt. necessary for the reaction to make the mixt. conductive, whereupon the reaction is carried on by heat derived from the elec. resistance of the mixt.

Preparation of solid peroxide combinations. HENKEL & CO. Ger. 302,735, Dec. 19, 1917. Peroxides are produced electrolytically at ordinary pressure and in commercial quantities by using, as electrolyte, solns. of alkalis or non-acid salts into which O or O-contg. gases are introduced with the addition of suitable sol. compds. such as water glass, starch, gelatin, albumin.

Basic magnesium hypochlorite. E. MERCK CHEMISCHE FABRIK. Ger. 297,874, May 24, 1917. MgCl_2 soln. is electrolyzed in the presence of MgO , $\text{Mg}(\text{OH})_2$, or MgCO_3 .

Electrolysis of potassium chlorate solutions. OBERSCHLESISCHE SPRENGSTOFF-ARTFABRIKESBESITZSCHAFT. Ger. 300,021, Nov. 26, 1919. KClO_3 solns. are electrolyzed with Ni cathodes at 27° and a c. d. of about 0.15 amp./sq. cm. to produce KClO_4 .

Electrolysis of water. E. BAUER. Ger. 345,048, Dec. 5, 1921. A quadrangular sheet-iron trough contains molten NaOH or KOH contg. 5–10% H_2O . Into this mass, which is heated to 350° or 300°, dip a number of right-angled narrow gas bells of sheet iron. The gas bells have insulated iron electrodes which are alternately connected to the positive and to the negative poles of a generator. A tube for the outlet of H or O gas is let into each bell and a second tube is let in for the introduction of steam, which is admitted in proportion as the products of electrolysis are withdrawn. The heat carried by the O and H is used in the production of the steam.

Conditioning gases. H. A. PROSSER. Can. 234,283, Sept. 18, 1923. In the elec. pptn. of suspended solid matter from a body of moving gases an acid fume is added to the gases at a point spaced from the elec. field, sufficient to render the particles conductive but not sufficient to cause the particles to become moistened.

Extracting zinc. DUNFORD & ELLIOTT (SHEFFIELD), LTD., and A. H. PETERSON. Brit. 195,382, March 20, 1923. In the extn. of Zn by distn. in an elec. furnace, the charge of ore and carbonaceous material is subjected to a preliminary heat treatment in a sep. chamber simultaneously with the reduction of the Zn, the condensation of the Zn vapor taking place in a movable condenser. A suitable construction is specified.

Electric incandescent lamps. JUST-FÉLE IZZÓLAMPÁ ÉS VILLA-MOSSÁGI GYÁR RÉSZVÉNYTÁRSÁG. Brit. 153,833, Feb. 12, 1923. To prevent blackening of vacuum and gas-filled lamps, the inner surfaces of the lamp parts are coated, either before or after they are assembled, with a layer of a reducing substance which is solid or liquid at 20° and volatile, at least in a vacuum, at glass-softening temp., such as P, sesquisulfide of P, or As selenide. The reducing layer is heated in a current of perfectly dry and inert gas after which the lamp is assembled and finished. In one method particularly applicable to vacuum lamps, Roentgen-ray tubes, Geissler tubes, etc., the lamp mount is coated with red P, the lamp exhausted and then filled with an inert gas after which the lamp is subjected to the full voltage so that the P evaps. and settles on the cool parts of the lamp. The current is then reduced and the lamp heated when the P is again evapd. and can be exhausted together with the gas. In the case of gas-filled lamps, the lamp mount may be coated with an ample quantity of P and finished in the usual way. The process is particularly applicable to gas-filled lamps with less than 50 mm. Hg pressure. Cf. C. A. 17, 694.

Electric incandescent lamps, etc. NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIEKEN, G. HOLST, E. OOSTERHUIS AND J. C. LOKKER. Brit. 194,198, May 9, 1922. Leading-in wires comprise a core of material that becomes plastic at the elastic limit and of high elec. cond. (e. g., Cu) surrounded by and in contact with an iron-alloy sheath, the composite wire having a coefficient of expansion equal to that of the vitreous material into which it is to be sealed. A wash of Cu or like metal may be applied to the outer surface of the composite wire to facilitate its adhesion to the vitreous material.

Metallic-vapor rectifiers. AKT.-GES. BROWN, BOVERI, ET CIE. Brit. 194,724, March 12, 1923. An auxiliary anode, which serves to ignite and excite the arc of a Hg or other metallic vapor rectifier, extends through and is insulated from a Hg cathode except at the upper end which lies close to the surface of, and is in contact with, the Hg, when the rectifier is not in operation.

6—INORGANIC CHEMISTRY

A. R. MIDDLETON

Action of selenium oxychloride on various metals and metallic oxides. W. L. RAY. *J. Am. Chem. Soc.* 45, 2090-4(1923). The temps. of reaction varied from room temp. to 90° (steam-bath); in some cases the reactions were studied at 275° (b. p. of SeOCl₂) or even higher. The material used included 9 metals, 9 metallic oxides and 2 selenides. Chloride of the metal, SeO₂ and, in some cases, Se₂Cl₂ were formed. Pb₂O₃ and PbO₂ also formed Cl₂. A new Cu acid selenite, CuSeO₃·SeO₂, green, cryst., was obtained by heating anhyd. CuCl₂ and SeOCl₂ in contact with air. Expts. indicated the reaction to be CuCl₂ + 3SeO₂ = CuSeO₃·SeO₂ + SeOCl₂, the SeOCl₂ acting merely as solvent for the SeO₂ formed by hydrolysis of SeOCl₂ by air moisture.

Composition of the precipitate from partially alkalinized alum solutions. L. B. MILLER. *U. S. Pub. Health Repts.* 38, 1995-2004(1923); cf. Williamson, C. A. 17, 2089; Theriault and Clark, C. A. 17, 1519. Varying aunts. of NaOH were added to alum solns. 0.005 and 0.02 molar in Al at room temp. and to the latter at 100°. After ppts. had settled 0.5 hr. the p_H value of the liquid was detd. colorimetrically. After centrifuging and decanting the ppt. was centrifuged with 200 cc. portions of water till nearly free from sulfate ion. At this point dispersion of the ppt. began. Bringing the p_H of the wash water to that of the soln. had little effect on the compn. of the ppt. For addns. of NaOH up to 2.5 mols. per mol. of Al at room temp., compn. of the ppt. was const. and approximated Williamson's 5Al₂O₃·3SO₃. Increasing concn. of SO₄ ion over a wide range (addn. of K₂SO₄ or (NH₄)₂SO₄) or increasing concn. of Al up to 0.1 M had no effect on the compn. of the ppt. formed at a definite p_H . For p_H 4.0-5.5 the ratio Al:SO₄ in the ppt. is const.; at higher p_H values SO₄ rapidly disappears or, practically, when 3 or more mols. of NaOH are added for each mol. of Al, the ppt. can be washed free from SO₄. The ppt. appears to consist of two components of nearly equal solv. For 0.005 M Al the greatest insolv. of the ppt. was found at p_H 6.7-7.0 at which point 2.75 mols. of NaOH have been added. On both sides of this, however, p_H 5.4-8.5, are zones of great insolv. Theriault and Clark's point of greatest flocculation, p_H 5.5 (2.1 mols. of NaOH added), is the point where pptn. of Al first approaches completion and is in the region where greatest SO₄ is found in the ppt. In Blum's method for detn. of Al it is essential that SO₄ be absent or present in small amt. If present in large amt. a second pptn. from HCl soln. is necessary. Chloride is satisfactorily removed by 10 min. ignition over a Meker burner. Expts. with AlCl₃ solns. had to be abandoned on account of formation of colloidal suspensions not flocculated by prolonged centrifuging.

A. R. M.

Oxidation of graphite with a mixture of silver dichromate and sulfuric acid. L. J. SIMON. *Compt. rend.* 177, 122-4(1923).—A pure sample of graphite which by org. analysis gave a C content of 99.9% was completely oxidized, or gasified in 0.5 hr. at a temp. not exceeding 100° by a mixt. of concd. H₂SO₄ and Ag₂Cr₂O₇. The values of the C content obtained this way were a little high (C = 102%), but this is explained on the basis of occluded H₂ in the graphite. When similar tests on the same material were carried out with CrO₃ and concd. H₂SO₄ the results gave only 73% of C, although these results vary with the conditions. S. finds that by the latter method about 0.16% of the C is in the form of CO, while when Ag₂Cr₂O₇ is used this will run as high as 1.7%. As equal vols. of CO and CO₂ contain practically the same quantity of C this does not affect the results. These expts. were repeated with samples of graphite of varying degrees of purity. The C was completely gasified by the mixt. of concd. H₂SO₄ and Ag₂Cr₂O₇.

but only about 66% in the cases where CrO_3 was used. The use of concd. H_2SO_4 and $\text{Ag}_2\text{Cr}_2\text{O}_7$ gives a method of *sepg. graphite from charcoal, coke and sugar carbon* which are only partially attacked by these reagents. R. G. FRANKLIN

Chemical constitution of bleaching powder. S. OCHI. *J. Chem. Ind. (Japan)* **26**, 1-14 (1923).—O. has measured the heat of soln. of bleaching powder and the vapor pressure of water in it, and has also made a microscopical examn. of the substance. The material used for the investigation was prepared from pure $\text{Ca}(\text{OH})_2$ by careful chlorination. The heat of soln. of bleaching powder of different water contents was measured, and from the results the mol. heat of soln. of $\text{Ca}(\text{OCl})\text{Cl}$ was calcd.; allowance was made for the heat effect produced by CaCl_2 present as an impurity, the water of crystn. of CaCl_2 being assumed to be 6 mols. There was a turning point in the curve at about 1 mol. of water to 1 mol. of $\text{Ca}(\text{OCl})\text{Cl}$. The heat of soln. of $\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$ was found to be 7530 cal., that of $\text{Ca}(\text{OCl})\text{Cl} \cdot 9830$ cal., giving 2300 cal. as the heat of hydration of $\text{Ca}(\text{OCl})\text{Cl}$. Air free from water and CO_2 was passed through the bleaching powder contg. 0.82 mol. of water per mol. of $\text{Ca}(\text{OCl})\text{Cl}$, the water vapor evapd. being collected in a CaCl_2 tube. The vapor pressure was then calcd., the following results being obtained: 7.99 mm. at 30° , 3.93 mm. at 20° , and 1.80 mm. at 10° . The heat of hydration calcd. from these data is 2260 cal. (from 10 to 20°) and 2000 cal. (from 20 to 30°). When observed under the microscope with nicols, bleaching powder moistened with tetrachloroethane appears as fine crystals showing double refraction. When the material contains water corresponding to the formula, $\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$, the double refraction is most distinct, and it vanishes when the material is dried or moistened with water. Among the fine crystals there are some amorphous masses, the surfaces of which are covered with fine crystals; these are considered to be unattacked $\text{Ca}(\text{OH})_2$. Bleaching powder newly manufactured does not show the distinct double refraction, but it appears after standing overnight. Moreover, the cryst. state depends largely upon the conditions of manuf. and the nature of the raw materials. From his results O. concludes that the principal constituent of bleaching powder is a compd., $\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$, of definite chem. compn., with water of crystn. and that Ca hydroxide or oxide is not present in the combined state but mechanically admixed. J. S. C. I.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Studies in adsorption. II. Adsorption of compounds and quantitative analysis. N. R. DHAR, K. C. SEN AND N. G. CHATTERJI. *Kolloid-Z.* **33**, 29-31 (1923); cf. *C. A.* **17**, 3436.—When a ppt. is formed in a soln. contg. a third electrolyte, the ppt. frequently adsorbs some of the latter from which it cannot be freed by thorough washing. This often makes repptn. necessary in analytical work. SrSO_4 pptd. in the presence of chlorides and sulfates of various metals and washed with dil. H_2SO_4 adsorbed Fe^{+++} in large amts., Al^{+++} and Cr^{+++} considerably, Ni^{++} , Co^{++} , and Cu^{++} slightly and Hg^{++} not at all. BaSO_4 and CaSO_4 ppts. adsorb Fe^{+++} . FePO_4 , AlPO_4 , and CrPO_4 ppts. adsorb Ca^{++} . $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ adsorb Zn^{++} , Cu^{++} , Ni^{++} , Cd^{++} and Ca^{++} but not Ag^+ . BaCO_3 , CaCO_3 and SrCO_3 adsorb Fe^{+++} and Mg^{++} . Ca citrate adsorbs Fe^{+++} . Fe benzoate adsorbs Ca^{++} . F. L. BROWNE

Calcium oxalate precipitation. A. H. ERDENBRECHER. *Mikrokosmos* **16**, 201-2 (1923).—Photographs indicate that better crystals are formed by pptn. from AcOH solns. than from NH_4OH solns. The following procedure is recommended. To an aq. soln. of 0.1-0.15 g. Ca in 75 cc., add 10 cc. concd. AcOH , heat to boiling and add slowly from a buret 7-10 cc. of a cold satd. soln. of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at the rate of 1 drop in 5 secs. Finally add a slight excess of NH_4OH . W. T. HALL

Studies on the determination of copper and its separation from cadmium. P. WENGER AND DÜRST. *Helvetica Chim. Acta* **6**, 642-7 (1923).— Cu can be detd. satisfactorily as CuO after pptn. with dil. alkali if a correction is made for the SiO_2 in the ppt. The classic method of weighing Cu as Cu_2S after ignition of the H_2S in H_2 is a good method and serves for the sepn. of Cu from Cd if 5 cc. of concd. H_2SO_4 is present in each 100 cc. of soln. treated with H_2S . When $\text{Na}_2\text{S}_2\text{O}_3$ is used as a precipitant some CdS is likely to be thrown down. The sepn. which depends upon the pptn. of $\text{Cu}_2(\text{CNS})_2$ gives low values for Cu . Perhaps the easiest method for sepg. Cu and Cd is based on pptn. with H_3PO_4 . By using 25% H_3PO_4 and washing the Cu deposited from the boiling soln. with water, alc. and ether successively, the results are very satisfactory. W. T. HALL

The determination of copper volumetrically by means of sodium sulfide. ARTURO

BORNTRAEGER. *Ann. scuola agr. Portici* [2] 16, 1-55(1920).—The Pelouze method for the titration of Cu, in ammoniacal soln., with Na₂S, carried out at ordinary temp. (Mohr), is capable of furnishing easily very exact results. Those other metals which under similar conditions are pptd. by sol. sulfides should naturally be absent. A good internal indicator is not yet known for the end point of the titration. The best method of fixing this consists in catching the precise point of the disappearance of the last trace of dissolved Cu. To do this it is preferable to add a little K₄Fe(CN)₆ to a test of the reaction liquid, filtered and acidulated by AcOH. Wishing, or having, for particular reasons, to pay attention to a certain excess of Na₂S, the use of the touch drop method with Pb preps., more especially basic acetate paper, is recommended. Na nitroprussiate is less suitable for this purpose and *p*-aminodimethylaniline still less so. The last is especially poorly suited in the case of the use of not well kept solns. of Na₂S, partially oxidized, contg. hyposulfate. The presence of this last, however, does not harmfully affect the reaction of sol. sulfides with Pb preps. or with Na nitroprussiate, nor that of Cu with ferrocyanide. The temps. of the room, occurring in practiced work, do not influence the results of the titrations (up to 43-50°). Solns. of Na₂S keep for a long time const. strength if preserved under a layer of petroleum in a room of moderate temp. and not too much illuminated.

ALBERT R. MERZ

A simple, rapid and economical method of separating nickel and copper from iron. E. G. R. ARDAGH AND G. M. BROUGHALL. *Can. Chem. Met.* 7, 198-200(1923).—Evap. the soln. to 2-3 cc., mix with 5-10 g. of NH₄ salt and add 5-10 cc. of concd. NH₄OH. Dil., filter and wash with *N* NH₄OH contg. 10% of dissolved NH₄ salt. Numerous values are given to show the accuracy of this method of sepn. and a bibliography of methods for detg. Ni and Cu is appended.

I. J. ROGERS

The separation of tin from other metals, including its determination after precipitation by means of cupferron. N. H. FURMAN. *Ind. Eng. Chem.* 15, 1071-3 (1923).—A satisfactory sepn. of Sn from Sb, Pb, Cu and As can be made in a soln. contg. 0.1-0.3 g. of Sn and corresponding wts. of the other cations in 500 cc. of soln. contg. 5 cc. of 48% H₂P₂, 4 g. H₃BO₃ (which prevents the action of H₂P₂ on glass), 5 cc. of concd. H₂SO₄ and 10 cc. of 12 *N* HCl. If the Sn is in the quadrivalent condition, none of it is pptd. by H₂S. In the filtrate the Sn can be pptd. by cupferron and the ppt. changed to SnO₂ by ignition.

W. T. H.

Gravimetric and volumetric methods for the estimation of tin in alloys. ANTONIN JILEK. *Chem. Listy* 17, 53-6, 85-7(1923).—The modification of Czerwek's method for the estn. of tin, described in a previous article (cf. *C. A.* 17, 2841), gives the best results for bearing metals when for alloys contg. 14-30% of tin, 0.5 g. is taken, for 30-75% of tin, 0.25 g. is taken, and for 75-100% of tin, 0.15 g. of alloy is used. If smaller quantities are used, low results are obtained, owing to incomplete pptn. of the tin, while larger quantities give high results, owing to adsorption of Sb salts on the stanniphosphate ppt. Classen's electrolytic method for the estn. of Sn was tested for bearing metals and gave satisfactory results with a current of 0.5 amp., for which *V* is 3.5. This method has the advantage over Czerwek's method and its modification of being more rapid. For type metal contg. about 2% of tin, the results obtained by the modification of Czerwek's method are lower than those by the iodimetric method, agreement being obtained commencing with alloys contg. more than 11% of tin. Below this, better results are obtained by using the unmodified Czerwek soln.

J. C. S.

The reaction between manganese, lead peroxide, and sulfuric acid. B. f. DIRMONT. *J. Russ. Phys. Chem. Soc.* 48, 1807-11(1916).—A modification of the Crum-Volhard reaction for the detection of Mn, which consisted in the addn. of the substance to be tested to a boiling suspension of PbO₂ in HNO₃, when a violet coloration is produced. It is shown that the substitution of dil. H₂SO₄ for HNO₃ in the above reaction enhances the delicacy of the reaction. This method is not suitable for quant. estns. as the max. amt. of Mn capable of being oxidized in this way to HMnO₄ is only 30%. Max. oxidation is obtained with 8-9% H₂SO₄, greater or smaller concns. causing a rapid decrease in the amt. of oxidation.

J. C. S.

The mechanism of the Crum-Volhard and of the Dyrmont reactions for manganese. N. A. VALYASHKO. *J. Russ. Phys. Chem. Soc.* 48, 1815-20(1916); cf. preceding abstr.—A comparative study is made of the above reactions for the detection of Mn. The Dyrmont modification of the Crum-Volhard reaction, which consists of substituting H₂SO₄ for the HNO₃ used in the latter, gives a much more intense coloration, which has the further advantage of being stable towards H₂SO₄, whereas the HMnO₄ produced by the Crum-Volhard reaction is decomposed by prolonged boiling with HNO₃. This decolorization is explained by Volhard, and by Morse (*Ber.* 30, 48-50(1896)), to be due to the pptn. of hydrated MnO₂, which is thus removed from the sphere of reaction.

Hydrated MnO_2 , however, gives the Crum-Volhard reaction for Mn, and the brown ppts. obtained by prolonged boiling of the reaction solns. in both cases are probably double compds. of PbO_2 and MnO_2 . These compds. are not identical, the compd. obtained from the Crum-Volhard reaction being more stable to acids than the substance obtained from the Dyrmont modification of this method, thus explaining the greater permanence of the coloration obtained by the latter. J. C. S.

Gravimetric determination of zinc. G. SPACU. *Bul. soc. stiinte Cluj* 1, 361-4 (1922).—Add a slight excess of NH_4CNS to a neutral soln. of a Zn salt, then add a few drops of pyridine slowly and with vigorous stirring. Collect the white ppt. of $\text{ZnPy} \cdot (\text{SCN})_2$ after 15 mins., wash with a cold soln. of 0.3 g. of NH_4CNS , 0.2 g. of $(\text{NH}_4)_2\text{SO}_4$, 100 cc. of water, dry, ignite over a Teclu burner, and weigh as ZnO . The method seps. Zn from Mg and the alk. earths. J. S. C. I.

The analysis of chrome-vanadium steel. G. E. F. LUNDELL, J. I. HOFFMAN AND H. A. BRIGHT. *Ind. Eng. Chem.* 15, 1064 9(1923).—*To det. Mn*, dissolve 1 g. of sample in exactly 20 cc. of 3.6 N H_2SO_4 . Dil. to 100 cc. and add 8% NaHCO_3 until a slight permanent ppt. is formed and then 4 cc. in excess. Boil 1 min., let settle and filter as rapidly as possible. To the filtrate, add 35 cc. of 7.5 N HNO_3 and carry out the usual bisulfate method for Mn. *To det. P*, dissolve the sample as in the analysis of ordinary steel. Cool the soln. to 15-20° and reduce V to 4-valent condition by FeSO_4 soln. and a little SO_2 aq. Ppt. with molybdate at 15-20° and allow 30 mins. for the ppt. to form. *To det. Cr*, dissolve 2 g. of steel in 60 cc. of acid which is 5.75 N in H_2SO_4 and contains 0.8% by vol. of sirupy H_3PO_4 . Oxidize with 10 cc. of 6 N HNO_3 , boil and add 2.5% AgNO_3 soln. until 0.3 g. AgNO_3 is present for each 1.5% Cr. Dil. to 300 cc. with hot water and, to the nearly boiling soln., add 8 cc. of 15% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ soln. Boil 15-30 mins., cool, add an excess of standard FeSO_4 soln. and titrate with 0.03 N KMnO_4 , allowing for diln. effect and color interference. *To det. V*, the method of the U. S. Steel Corp. chemists is recommended. W. T. H.

Contribution to unification of methods of analysis of cast irons and common steels. GIUSEPPE TOMARICINO. *Met. italiana* 15, 324-31(1923).—Proposed specifications for reagents and app., and description of methods are given for the following: total C, graphitic C, combined C, Si, S, P, Mn, As and Cu. ROBERT S. POSMONTIER

Estimation of cobalt in special steels. GIULIO FERRERI. *Giorn. chim. ind. applicata* 5, 330-40(1923).—Treat 2 g. steel filings with dil. HNO_3 , wash to dryness and ignite to decompose nitrates. Moisten with a little concd. HCl , then take up with HNO_3 (d. 1.12), warming slightly. Bring to dryness again, moisten with concd. HCl , and take up with dil. HCl , heating without boiling. All the oxides dissolve except WO_3 and SiO_2 . Cone. to sirupy consistency, allow to cool, dil. with H_2O , allow to stand a few min., filter and wash with H_2O acidulated with HCl . Reserve filtrate A for Co. In the ppt. (made up of WO_3 and SiO_2 together with small amts. of Fe, Mn, Cr and Co) det. SiO_2 by difference with HF , and W, also by difference, after fusing the residue with KNaCO_3 and lixiviating with H_2O . Alk. tungstates pass into soln. Dissolve the slight residue in a little HCl , and add the solns. to filtrate A. Evap. the combined filtrates as much as possible without sepn. of salts, take up with 60-70 cc. H_2O . (If desired, treat the cold soln. with AcONa at this point to avoid decompn. of a part of the NaNO_3 , although if the evapn. has been conducted properly the development of nitrous vapors will not cause inconvenience.) Acidify with AcOH , treat, while stirring, with an excess of a concd. soln. of pure KNO_3 , to which are added a few drops of AcOH . A ppt. of K cobaltinitrite forms at once. Allow to stand 12 hrs., filter, wash with 5% KNO_3 contg. a few drops of AcOH . Place the ppt. with filter in the pptg. beaker, dissolve with a little HCl in the warm, filter into a dish, add 3-4 drops H_2SO_4 and heat to white fumes on the sand bath to drive out HCl . If during this operation the liquid turns black with sepn. of salts, add a few drops of aqua regia and continue the evapn. After cooling take up with H_2O and NH_4OH , bring to about 100 cc. with 15 N NH_4OH , add 5 g. $(\text{NH}_4)_2\text{SO}_4$ and electrolyze, using Winkler electrodes, at ordinary temp., with current density of 0.7-1.0 amp. Sometimes small amts. of Fe, Cr, etc., sep. in the ammoniacal soln. They do not disturb the electrolysis and filtration is not necessary. The results are very satisfactory. ROBERT S. POSMONTIER

Rapid methods for estimating carbon in steels and cast irons. I. MUSATTI AND M. CROCE. *Giorn. chim. ind. applicata* 5, 225-33(1922).—(1) Method of Mahler and Goutal, consisting in rapid combustion in O under compression. This method is somewhat complex in practice. (a) In order that steel should burn completely it is necessary that, at the end of combustion, the internal pressure in the bomb should not go below certain detd. limits, which depend upon the nature and quantity of the metal used. (b) In cast irons and ferro alloys there must be added, besides the oxidizing substance

(PbO₂), also some low-C steel to favor the combustion of the charge. This assumes a knowledge of the C content of the auxiliary steel and necessitates an additional weighing. (c) The complete absorption of the resulting CO₂ and the successive washings of the bomb with air or O to expel all the residual CO₂ are long and delicate operations. (d) The suggestion made (in order to save time) not to expel all the gas from the combustion, but to note the final manometric pressure and to discharge an aliquot part of the gas whose CO₂ content can be detd., would not give accurate results, because of the inaccurate indications of the manometer. (e) No account is taken of error due to combustion of S, which may be absorbed as SO₂ or SO₃, giving high results for CO₂. (f) The method has no particular advantages to justify the expenditure of 30–40 min. required. (II) Combustion in an O current. The authors have made a few modifications in the elec. furnace, details of which are given. (a) Gas volumetric measurement of the CO₂. Great exactness and speed are not obtainable for the following reasons: (1) The measurement of the gas over H₂O is affected by well known errors, negligible in tech. but not in exact analysis. (2) Since small amts. of metal are used, requiring relatively small quantities of O because of the limited capacity of the graduated buret, thorough washing of the app. to expel last traces of CO₂ cannot be carried out. (3) The min. time for all operations cannot be less than 10 min. (b) The gravimetric method of Stetser and Norton gives satisfactory results but is not particularly rapid. (c) Volumetric method of Cain. This method is not particularly exact or rapid, and the technic offers a no. of difficulties and inconveniences. (d) Phys. method of Cain and Maxwell. This method is very good, simple and quick, but is not readily adaptable for ordinary practice, requiring costly and fragile app. and skillful operators. (III) Direct titration method, after combustion in elec. furnace. Complete details are given with photographs and sketches of app. The results are very exact and the method is applicable to ordinary and special steels and to cast irons, but not to ferro alloys. One analysis requires 12–15 min., but with 2 operators working simultaneously at the same app., 7 or 8 analyses may be made per hr. (IV) Rapid detn. of graphite in cast iron. The authors modify the usual method by filtering the residue from the acid treatment in a Gooch or aluminum crucible, washing and drying, then burning in a special elec. furnace and proceeding as in their method above.

ROBERT S. POSMONTIER

A new gravimetric determination of nitric acid. H. RUPE AND P. BECHTER. *Helvetica Chim. Acta*, **6**, 674–6 (1923).—A 10% soln. in 50% AcOH of the acetate of di(1-naphthylmethyl)amine is a sensitive reagent for HNO₃. The ppt. should be formed in 200 cc. of boiling soln. contg. 2–10 cc. of 10% H₂SO₄ and HNO₃ equiv. to 0.1 g. KNO₃. H₃PO₄ and H₂SO₄ do not interfere but other mineral acids should be absent.

W. T. H.

Separation of phosphoric acid from hydrofluoric acid. E. MÜLLER AND W. WAGNER. *Z. anorg. allgem. Chem.* **129**, 306–8 (1923).—In the analysis of bauxite it was found that pptn. of H₃PO₄ as Ag₃PO₄ from a soln. carefully neutralized by HNO₃ was incomplete. Expts. with Na₂HPO₄·12H₂O showed that a quite constant amt., 0.0374 g. per 0.1 g. of salt, escaped pptn. in consequence of the increase of hydron during pptn. If the filtrate was neutralized with 0.1 N NaOH to the turning pt. of methyl orange, the additional Ag₃PO₄ contained some Ag₂O. The following procedure gave good results. To the alk. reacting soln. add AgNO₃ in slight excess with vigorous stirring and 1–2 drops of methyl orange; make just alk. with 0.1 N NaOH, then just acid with 0.05 N HNO₃. Heat on water bath 30 min. protected from light, filter, wash free from Ag, dry at 90°, place ppt. sepd. from filter in weighed porcelain crucible, dissolve remaining ppt. on filter with hot dil. HNO₃, filter, add soln. to crucible, evap. to dryness on water bath, remove HNO₃ by small flame and ignite to dark redness.

A. R. MIDDLETON

The titration of hydrofluoric and hydrofluosilicic acids in mixtures containing small amounts of hydrofluosilicic acid. P. H. M. P. BRINTON, L. A. SARVER, A. LONDON AND A. E. STOPPEL. *Ind. Eng. Chem.* **15**, 1080–1 (1923).—Scott has described a method for the analysis of such mixts. by titrating H₂F₂ and H₂SiF₆ in the cold with phenolphthalein as indicator and then at 80° with the same indicator. If this method is to be used, care should be taken to det. the amt. of dissolved SiO₂ in the NaOH soln. This reacts with H₂F₂ to form H₂SiF₆. Special precautions are also necessary in weighing out the sample.

W. T. H.

The iodometric determination of small quantities of cyanide and thiocyanate. E. SCHULZE. *Z. anal. Chem.* **62**, 337–42 (1923).—In a slightly acid soln. of alkali cyanide and thiocyanate Br₂ aq. reacts quantitatively as follows: HCN + Br₂ = CNBr + HBr; KCN + 4Br₂ + 4H₂O = H₂SO₄ + 7HBr + CNBr. The CNBr is quite stable in faintly acid solns. By treatment with phenol the excess Br₂ can be removed. Then the CNBr can be made to react with HI, CNBr + 2HI = HCN +

HBr + I_2 , and the liberated I_2 titrated with thiosulfate. To 50 cc. of soln. contg. 0.1–40 mg. HCN and 0.3–90 mg. HCNS in a 120-cc. glass-stoppered flask, add 5 cc. of 20% H_3PO_4 , and introduce dropwise enough Br_2 to color the soln. distinctly yellow. Afterwards add 30–40 drops of 5% phenol soln. Shake well and after 15 min. add 0.5 g. KI and allow the mixt. to remain in the dark for 30 min. before titrating with $Na_2S_2O_3$ soln. To sep. HCN and HCNS, treat the mixt. of alkali cyanide and thiocyanate with 1 g. of H_2BO_3 and distil through a ground-glass connection and a glass tube drawn on into a narrow tube at the end into a small receiver contg. water and about 1 cc. N NaOH. After a few min. all of the cyanide will be in the receiver and the HCNS will remain in the original flask. W. T. HALL

New reagents for the investigation of hydrocyanic acid. JUAN PESET and JAVIER AGUILAR. *Arch. med. legal* 1, 18–21 (1922); *Chem. Zentr.* 1923, II, 223–4.—In the reaction of Pagenstecher and Schönheim (the turning blue of guaiacum resin- $CuSO_4$ paper) the Cu ion is indispensable. On the contrary, tincture of guaiacum can be substituted by other chromogenic oxidation reagents such as benzidine, dimethyl- p -phenylenediamine, pyrimidine, aloin and fluorescein in alk. soln. A few other compds. such as p -dianilino-diphenylamine and tetramethyl- p -phenylenediamine give, even without HCN, similar, though paler, colors than those which appear in its presence. C. C. DAVIS

A new method of analyzing sodium byposulfite. S. H. WILKES. *J. Soc. Chem. Ind.* 42, 356–7T (1923).—When a neutral soln. of $Na_2S_2O_4$ is treated with an excess of KIO_3 , KI and a measured vol. of standard $Na_2S_2O_3$ soln., a series of reactions take place which can be summarized as follows: $3Na_2S_2O_4 + 4KIO_3 + 2KI = 3I_2 + 3Na_2SO_4 + 3K_2SO_4$; $3I_2 + 6Na_2S_2O_3 = 3Na_2SO_4 + 6NaI$. The excess of 0.1 N $Na_2S_2O_3$ can be detd. by iodometric titration. Place 500 cc. of water, at least 6 g. of KIO_3 and 10 g. of KIO_4 in a 1. measuring flask. Add 300 cc. of 0.1 N $Na_2S_2O_3$ and a weighed quantity of the $Na_2S_2O_4$ sample. Dil. up to the mark, mix and titrate 100 cc. portions with 0.1 N I_2 soln. To avoid losses and decompn. of the sample, transfer with a spatula from the stock bottle to a weighing bottle and do not pour from one to the other. Weigh the sample and container. Place a short, wide-necked, dry funnel in the neck of the measuring flask, invert the weighing bottle over this and transfer the sample to the flask. In doing this, incline the flask and funnel to meet the weighing bottle so that the latter fits well down into the funnel and when the bottle is inverted, the funnel seals its mouth completely. Then weigh the empty bottle. The above method of analysis is not applicable in the presence of Na_2CO_3 or decompn. products of $Na_2S_2O_4$. W. T. HALL

Detection of nitrates in plant and animal material. TH. SABALITSCHKA and C. SCHMIDT. *Ber. pharm. Ges.* 33, 181–4 (1923).—The procedure is as follows: On a watch glass just aside the center place a minute quantity of the sample and opposite beyond contact a few drops of concd. H_2SO_4 . On a similar watch glass place the smallest possible droplet of Ph_2NH reagent (a few crystals of Ph_2NH dissolved in 1–2 cc. of concd. H_2SO_4), cover and tilt the pair so that the org. material gradually becomes soaked with acid. If nitrates are present the Ph_2NH reagent develops a blue color. In mixtures of HNO_3 with iodide and bromide, an observation is made only after the expt. has continued some 10 to 20 min. Chromates or chlorides alone offer no interference to the procedure, only in the event of their simultaneous occurrence is it necessary first to eliminate the former, to which end the sample in minute quantity is warmed with 5 cc. of 5% HCl at about 50°. $PbCO_3$ added, the mixt. boiled, and after cooling filtered. To the filtrate add neutral $Pb(OAc)_2$ until no further ppt. is formed. Filter and evap. filtrate along with a small quantity of basic $PbCO_3$ to dryness on a H_2O bath, stirring from time to time in order to favor the formation of a pulverulent mass, which is thereupon examd. for HNO_3 as above described. W. O. EMERY

A new reaction of ketones. C. GILLET. *Bull. soc. chim.* 33, 465–6 (1923).—In 1899 G. published a note to the effect that cryst. ppts. could be obtained in dil. solns. of ketones by means of an excess of Nessler reagent and this paper was evidently overlooked by Bougault and Gros (*C. A.* 16, 3281). W. T. HALL

The effect of soluble calcium salts on the estimation of dextrose and its cause. WILHELM BIEHLER. *Z. Biol.* 77, 59–72 (1922).—In the estn. of dextrose by means of Fehling's soln., low results are obtained if sol. Ca salts are present, the error being approx. proportional to the quantity of Ca. Sol. salts of Ba and Sr, but not of Mg, Zn, or Li, act similarly. This loss of reducing power is probably caused by the partial conversion of the dextrose into saccharinic acid under the influence of the alk.-earth hydroxides. J. C. S.

The action of metallic sodium on α - and β -naphthol, and the application of the sodium reaction for the detection and distinction of these two phenols. HERMANN KUNZ-KRAUSE. *Chem.-Zig.* 47, 646 (1923).—A small quantity of the substance for

analysis is dissolved in a little abs. alc., the container is cooled in water, and Na in thin pieces added as long as it will dissolve. No pptn. takes place with either α - or β -naphthol, in the α -naphthol only a slight bluish green coloration and a scarcely perceptible fluorescence are seen, whereas with β -naphthol a deep Prussian blue coloration and very characteristic fluorescence appear. Although the color changes to olive, brown and finally orange, the fluorescence remains throughout. In evapn. even mechanically pure α -naphthol very small admixts. of β -naphthol can be detected easily. W. C. KUATZ.

Some methods for detecting chondrin in gelatin. M. A. RAKESIN. *Chem.-Ztg.* 47, 602(1923).—Chondrin has a harmful influence on gelatin, especially when an optically clear gelatin is desired for use in photography. A small amt. of chondrin will make a gelatin soln. opalescent. To test for chondrin in gelatin treat a 10% soln. with chrome alum; if chondrin is present the soln. will gelatinize while hot. After a soln. of chondrin has been treated with a soln. of $\text{Al}(\text{OH})_3$ the filtrate will give a reaction with BaCl_2 . Another method consists in treating a soln. with BaCl_2 and H_2SO_4 and getting the $[\eta]$ of the soln. E. J. KERS.

A method for the determination of toluidine. S. PALKIN. *Ind. Eng. Chem.* 15, 1045(1923).—Dissolve 0.5–1.0 g. of sample in N HCl and salt out toluidine dihydrochloride by adding 10 times as much satd. brine. Filter, dissolve in hot water and add 0.1 N NH_4OH until a slight excess is shown by methyl red. Filter and titrate the excess NH_4OH with 0.1 N HCl using methyl red as indicator. W. T. H.

DANTHINE: Guide pratique pour l'analyse des produits chimiques et alimentaires et la recherche des falsifications, suivi d'un Aide-Mémoire de chimie minérale et analytique. Paris: Gauthier-Villars et Cie. 156 pp. Fr. 10.

LAWSON, W.: Supplementary Notes on Gravimetric Analysis for Beginners. London: Longmans, Green & Co. 58 pp. 2s. 2d. Reviewed in *Pharm. J.* 111, 223(1923).

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

The occurrence of sphalerite and galena at Robilante (valley of the Vermeigne, Maritime Alps). A. BOCCATI. *La Miniera Ital.* 7 (1922); *Rev. Géol.* 4, 432(1923). Galena and sphalerite form rounded concretions, arranged in regular alignment like a string of beads, in a quartz gang. A nucleus of sphalerite is surrounded by a shell of galena. E. F. H.

The formation of hematite in a pottery furnace. M. BELLIERE. *Ann. soc. géol. Belg.* 47, 174–7(1919); *Rev. Géol.* 4, 297(1923). Small lamellar crystals of hematite were formed at the mouth of a covered porcelain crucible which had been in a pottery furnace during one burning. They were produced by a reaction between the vapors of H_2O and FeCl_3 , the latter being formed by the salting of the furnace. E. F. H.

The hematite occurrence at Rudki near Slupia Nowa. J. SAMSONOWICZ. *Compt. rend. serv. géol. Pologne* No. 4, 9–11(1922); *Rev. Géol.* 4, 267(1923). A vein of specular hematite fills a fissure in dolomite. E. F. H.

The feldspars and the methods of Fedorov. R. SABOT. *Bull. soc. franc. mineral.* 45, 97–129(1922).—The paper notes simplifications of Fedorov's methods, followed by a discussion of the types of feldspar twins, and the application of the method in detg. the compn. of feldspars. In plutonic grano-dioritic rocks the usual twins are of the albite and Carlsbad types; in plutonic gabbro-peridotitic rocks, pericline; the Mauebach, Esterel-Ala, Baveno and pericline twins occur in the alk. effusive and dike rocks. Within a rock the compn. of different crystals may vary 10% *An*. The feldspars are frequently zoned, varying in compn. A large number of illustrative detns. by the method are given. E. F. H.

The garnets of Bastogne and Salm-Chateau. H. BUTTENBACH. *Ann. soc. géol. Belg.* 45, B249–60(1922); *Rev. Géol.* 4, 129(1923).—At Bastogne two types of garnet occur in metamorphic rocks: one isotropic, the other anisotropic and composed of biaxial pyramids. Their compn. is $\text{CaFeMnAl}_2\text{Si}_2\text{O}_{12}$. At Salm-Chateau the garnet is isotropic spessartite. E. F. H.

The presence of carnotite in the Congo. A. SCHNEP AND E. RICHEL. *Bull. soc. belge Géol. Paléont. Hydrol.* 32, 150–2(1922); *Rev. Géol.* 4, 297(1923).—A yellow crystalline powder from a red calcareous sandstone at Katanga is identified as carnotite. E. F. H.

The presence of a very fusible substance in the interior of a quartz crystal from

a coal formation. M. BELLIERE. *Ann. soc. géol. Belg.* **47**, 197-9(1919); *Rev. Géol.* **4**, 297(1923).—A crystal of quartz contained a vacuole filled with a yellow substance, m. 25°, apparently a hydrocarbon. The substance included an air bubble. E. F. H.

The iron ores of the district of Opoczno. CZESLAW KUZNIAR. *Compt. rend. serv. géol. Pologne No. 2*, 1-2(1922); *Rev. Géol.* **4**, 267(1923).—Argillaceous siderite and oolitic Fe ore deposits are described. E. F. H.

The iron ores of Terre-Neuve. J. LEVAINVILLE. *Ann. Géogr.* **31**, 287(1922); *Rev. Géol.* **4**, 328(1923).—There are estd. to be 3635 million tons of hematite, partly submarine, in Terre-Neuve. The mean compn. is 54% Fe, 10% SiO₂, and 0.7% P. E. F. H.

The mining district of Colquimbo, province of Huarochiri, Peru. AURELIO MASIAS. *Informac. Mem. Soc. Ing. Peru* **24**, 369-75(1922); *Rev. Géol.* **4**, 171(1922).—This is a Cu district. It is described geologically. E. F. H.

A superficial ferruginous formation, called "grison," in the Armorica. F. KERFORNE. *Bull. soc. géol. minéral. Bretagne* **2**, 108-11(1921); *Rev. Géol.* **4**, 136(1923).—An agglomerate, composed of fragments of underlying rocks cemented by Fe and Mn oxides, is found beneath the vegetable mold. The Mn content reaches 13%. Generally Fe runs from 9 to 24%, but at Briquerville (Manche) it constitutes an ore, with 47%. E. F. H.

The argentiferous lead mines of the Côtés du Nord. E. CHRÉTIEN. *Bull. soc. géol. minéral. Bretagne* **2**, 520-6(1921); *Rev. Géol.* **4**, 260(1923).—Chiefly a historical study of the mines at Trémuson, Coat-an-Noz, Carnoët and Plusquellec. Analyses of ores are given. E. F. H.

The gold mine of Beslé (Lower Loire). F. KERFORNE. *Bull. soc. géol. minéral. Bretagne* **2**, 177-81(1921); *Rev. Géol.* **4**, 260(1923).—Native Au, pyrite and auriferous arsenopyrite form a vein in schist at Beslé. E. F. H.

Note on the geology and mineral deposits of the Umtali gold belt. A. B. V. ZEAL-LEW. *S. Rhodesia Geol. Survey Short Rept. No. 2*, 1-5(1918); *Rev. Géol.* **4**, 169(1923).—Deposits of sulfides, rich in Ag and low in Au, with or without quartz, occur in a narrow schist belt lying between two large masses of granite. Other types of deposits are "schist reefs," either rich or poor in sulfides, and Au-quartz veins low in sulfides. E. F. H.

Physicochemical examination of gold nuggets in relation to their genesis. S. F. ZHEMCHUZHNI. *J. Russ. Phys. Chem. Soc.* **54**, 5-28(1923).—The existence of gold-silver nuggets of practically const. compn. of 30-43% Ag (electrum) and 72-80% Ag (enstellite), with hardly any intermediate compns. between the latter and the pure metals, makes their crystn. from a molten state seem improbable. Z. aimed to investigate the possibility of the gold-silver nuggets' formation from natural solns. Three different solns. were made by mixing together two saturated aqueous solns. of NH₄Cl, one of them being satd. with AgCl, the other containing a provisory amount of NH₄AuCl₄. The concns. of Ag were kept constant at 0.1 g., per 100 cc. soln., the concns. of Au varied from 0.219 to 0.342 g., the actual proportions of the metals being 32.03; 24.82; and 23.83% Ag. Preliminary expts. with dextrose or urea reduction proving of no value, the reduction with Hg was finally resorted to. Reductions proceeded by steps, the ppts. of each step being examd. for Au and Ag and tabulated. It was found that Ag is reduced 7 times slower, so the natural solns. of both metals must deposit first crystals high in Au, with a comparatively non-varying content of Ag. The resulting enriched soln. of Ag will ppt. crystals of a different but also little varying compn. Three different nuggets from Ural mountains were analyzed and tested for their Brinell hardness in the natural, the annealed (600°) and the melted then slowly cooled state. One was subjected to pressure hardening after annealing.

	No. 1 (4670 g.)	No. 2 (3954 g.)	No. 3 (92 g.)
Gold	92.46	89.25	79.3
Silver	6.82	9.30	17.3
Copper	0.23	0.50
Impurities	0.3	0.70	0.8
Natural hardness tested. (100 kg.) pressure.	33.0	44.5	34.0
Hardness calcd. for mixt. of Au and Ag.	19.25	19.6	20.5
Hardness when annealed	19.2	19.5	20.8
Hardness, melted and slowly cooled	26.5	28.0
Hardness after pressing with 1240 kg./cm. ²	38-42
Structure after etching with aqua regia.	No polyhedra of solid solns.		

It is concluded that: nuggets of gold are formed by a simultaneous reduction of Ag-Au

sols. under the action of substances acting either directly or catalytically, and in the presence of primarily crystd. particles of magma An. They were afterwards subjected to deformation by high pressure of a magnitude easily produced either during dislocation processes in the earth's crust (primary origin), or by continuous shocks ensuing when the nuggets are carried down in mountainous streams (placets).

Investigations in the structure of platinum nuggets. S. F. ZUECHUZANI. *J. Russ. Phys. Chem. Soc.* 51, 417-60(1919).—I. Muchin in 1812 tried to classify the minerals of the Pt ores by their magnetic properties, relation to HCl, color, sp. gr. and chem. compn. V. I. Vernadskii, G. I. Chernik, and others continued the researches along the given direction, but obtained no results of a positive value for the problem of the genesis of Pt, and of the structure of its grains. Z. proceeded to study the problem by examn. of 14 nuggets of different sizes and from various sources have shown, that: (1) All nuggets are crystn. products from a molten magma. (2) The order of crystn. was: (a) osmiridium, (b) chromite, (c) a solid soln. of Pt with other Pt metals, also Fe, Cu, and Ni, and (d) olivine. (3) The nature of the solid soln. is apparent from the polyhedral microstructure of the Pt mass. (4) The Pt mass represents the α -ferro-platinum, otherwise called α -polyxene. (5) The hardness of the nuggets varies from 108 to 125 Br, and is reduced by annealing to 86-88 Br. (6) The hardness of the reconstituted Pt mass corrected for Fe losses and of synthetic α -ferro-platinum of the same compn. is also 86 Br. (7) Pt nuggets undoubtedly underwent a large amt. of hardening by pressure and other forces, working in the earth's crust. (8) Most of the nuggets contain a skeleton of chromite, and the Pt mass, being a secondary cryst. product, becomes allotrimorphic to chromite. (9) The purest samples crystd. in the absence of chromite and show a less affected structure. They almost always contain grains of secondary olivine, and of osmiridium which crystd. before Pt, but was of no influence upon the latter's form. (10) The initial magma contained gases, which were liberated during the crystn. of the nuggets, producing holes and cavities. (11) These gases did not include O, as the grains of osmiridium show no traces of oxidation. The paper contains 21 old analyses of Pt ores, 15 analyses of Pt nuggets and 18 photographs of microstructures.

Platinum assays and platinum promotions. S. C. LIND, C. W. DAVIS and M. W. von BERNOWITZ. *Bur. of Mines, Repts. of Investigations* 2496, 21 pp.(1923).—Ores and sands from various regions of the U. S. have revealed Pt to some assayers, but none has been detected in the same rock by others nor by the Bur. of Mines, though Pt always exists in such form that it can be detected quantitatively by regular methods. For several yrs. only a few hundred oz. have been recovered from ore, and in all cases Cu, Au or other metals were present in profitable amts. so that Pt was only a by-product. Prospecting by private and government agencies, including drilling of gravels and rocks, has shown only traces of Pt, and to work placers or alluvial sand for Pt alone would be unprofitable. Russian and Colombian Pt comes from gravel and none from ore. The occurrence of Pt in various countries and a list of numerous alleged deposits in the U. S. are included, with references to more detailed works.

The occurrence of platinum in southern Rhodesia. A. E. V. ZEALLEY. *S. Rhodesia Geol. Surv. Short Rept.* No. 3, 1-6(1918); *Rev. Géol.* 4, 169(1923).—Small quantities of Pt were contained in the concentrates from segregations of magnetite and chromite in serpentinized dunite.

Platinum metals in the Somabula diamondiferous gravels. H. B. MAUFE. *S. Rhodesia Geol. Surv. Short Rept.* No. 5, 1(1919); *Rev. Géol.* 4, 169(1923).—A concentrate obtained in washing gravels for diamonds showed 3 oz. 12 dwt. of Pt and 7 oz. osmiridium per ton.

Report on the tungsten deposits of Essersvale, Umzingwane district. A. E. V. ZEALLEY. *S. Rhodesia Geol. Survey Short Rept.* No. 1, 1-4(1917); *Rev. Géol.* 4, 171(1923).—Wolframite and scheelite occur in greisen veins in hornblende granite. Sixteen reefs are known which became valuable under war conditions.

Tungsten ores in southern Rhodesia. H. B. MAUFE. *S. Rhodesia Geol. Survey Short Rept.* No. 4, 1-4(1918); *Rev. Géol.* 4, 172(1923).—Wolframite and scheelite, found in Rhodesia, are described. The Rhodesian localities are listed, with the mode of occurrence in each. Hints for concn., and the relation of sales price of W ore to its assay value are discussed.

Norwegian arsenic ores and arsenic production. C. BUGGE and S. FOSLIE. *Norg. Geol. undersøkelse* No. 6(1922).—A thorough review of all the Norwegian As ore deposits and mines. Careful descriptions and some analyses are given. Of particular interest are some *Au detns.* showing that "pure" arsenopyrite may contain 30-60 g. Au per ton. A piece of ore was sepd. into its main constituents and each of these analyzed for As.

They contained: arsenopyrite, 33 g.; pyrite, 6 g. Au per ton; and the quartz only traces. The Au seems to follow the arsenopyrite in the sepn. A temporary miniature plant for As production put up by Statens Raastofkomite during the war is described. The raw material was arsenopyrite with 17-20% As. The resulting raw As contained about 86% As_2O_3 . The possibilities of a national As production from domestic ores are considered.

A mineral which all prospectors should know: betafite. L. DUMAS. *Bull. Mines Madagascar* Feb. 1923; *Rev. Géol.* 4, 432(1923).—The physical properties of betafite, an important pegmatite radioactive ore, are given.

The geology of the Lomagundi mica deposits. H. B. MAUFE. *S. Rhodesia Geol. Survey Short Rept. No. 10*, 1-8(1920); *Rev. Géol.* 4, 165(1923).—Muscovite occurs in pegmatite dikes, which intrude mica schist. The mica is found against the schist walls. The workings are described.

The occurrence of white mica (muscovite) in Roumania. D. ROTMAN. *Ann. Mines Roumanie* 5, 1-18(1922); *Rev. Géol.* 4, 166(1923).—The occurrences here described are in the valley of Măneasa in the southern Carpathians. The mica forms pockets at the contact between pegmatite veins and mica schist. One occurrence was mined by the Germans in 1917. The mineral is very pure, free from objectionable inclusions, clear, and forms sheets up to 20 X 20 cm.

Note on the bituminous schists of Estonia. R. ANTHOINE. *Ann. soc. géol. Belg.* 45, 224-6(1922); *Rev. Géol.* 4, 439(1923).—Volatile matter varies from 45 to 55%. Elementary analyses are given. The thickest bed is 2.5 m.

Petrological investigations of the grano-dioritic rocks of Süd-Ostbothnien. HEIKKI VÄYRYNEN. *Bull. Comm. Géol. Finlande* No. 57, 78 pp.(1923).—Two series of grano-dioritic rocks occur in Süd-Ostbothnien. The older series is composed of plagioclase, microcline, quartz, biotite and hornblende, which are stable together. The younger series contains several minerals which do not occur together in stable combinations. Chem. reactions between 2 or more minerals of the magma were indicated in numerous cases, and probable equations are presented. The application of the phase rule with respect to reactions between plagioclase, cordierite, almandine, hypersthene and diopside is discussed. The variation in the younger series is due to their intrusion into a cool part of the crust. An analysis is given of an amphibole near barkevikite but with lower alk. content.

An unusual rhyolite from the Blackall Range, southeastern Queensland. H. C. RICHARDS. *Proc. Roy. Soc. Queensland* 34, 195-208(1922); *Rev. Géol.* 4, 214(1923).—This rhyolite is very acid, with over 85% SiO_2 , and only 5 1/2% Al_2O_3 . Heated magmatic waters containing SiO_2 and CO_2 probably altered the original rhyolite during the last stages of cooling of the lava.

The quartzite of Kallio Kangas, its ripple marks and mud cracks. H. BERGHELL and V. HACKMAN. *Bull. Comm. Géol. Finlande* No. 59, 19 pp.(1923).—This paper includes an analysis of the quartzite from Kallio Kangas in northern Finland. A number of thin sections are figured.

The pozzuolana of the island of Vulcano. A. ROCCATI. *Le Miniere Ital.* 6, 331-38(1922); *Rev. Géol.* 4, 381(1923).—A phys. and chem. description.

Note deduced from Clarke's Data of Geochemistry; a proposition which concerns the genesis of metamorphic formations. DUMAS. *Bull. soc. franc. minéral.* 45, 129-32(1922).—D. gives Clarke's mean analyses (SiO_2 , Al_2O_3 , CaO and alk.) of metamorphosed sedimentaries, shale, sandstone and limestone. From this he calcs. the relative proportions of the 3 sediments needed to give the av. metamorphosed sedimentary rock; having 4 equations (one for each constituent) with 3 unknowns (the amts. of each sedimentary type). The av. compn. of the sedimentary lithosphere is calcd. to be: shales, 92 ± 4%; sandstones, 5 ± 1%; limestones, 3 ± 1%.

Description of an occurrence of salt now being formed, and theories relative to old occurrences of rock salt and potash salts. M. DEGOUTIN. *Ann. Mines Fr.* pt. 7, 1922, 5; *Rev. Géol.* 4, 259(1923).—Salt is now being deposited in the Assal lake on the French Coast of Somali. The lake is in a desert region where the temp. varies from 25° to 40°. It is 150 m. lower than sea-level and 10 km. distant from the ocean. The lake is fed by salt water springs through seepage from the ocean. The western half of the basin is solid salt, while the eastern half contains brine of 25° Baumé satn. A ring of gypsum surrounds the lake, deposited where the mixture of spring water and lake brine was at the proper concn.

Contribution to the explanation of the elevated temperatures in the Oberelsass potash beds. B. BUSCH. *Kali* 17, 202-3(1923).—At a depth of 500-600 m. the temp. of the Oberelsass K deposits is 6-10° higher than that of the central German deposits.

The theory is advanced that the higher temps. in the former are due to the insulating properties of interbedded layers of clay. K. D. JACOB

Radium minerals of Belgian Congo (SCHÖER) 3.

COLE, L. HEBER: *Silica in Canada; Its Occurrence, Exploitation and Uses*. Pt. I. Eastern Canada. Canada Dept. of Mines. Ottawa: Government Printing Bureau. 126 pp.

LOUIS, HENRY: *Mineral Valuation*. London: Griffin. 291 pp.

SCHNEIDERHÖHN, HANS: *Anleitung zur mikroskopischen Bestimmung und Untersuchung von Erzen und Aufbereitungsprodukten besonders in auffallenden Licht*. Berlin: Gesellschaft Deutscher Metallhütten und Bergleute. 292 pp. Reviewed in *Econ. Geol.* 18, 604(1923).

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST AND ROBERT S. WILLIAMS

The reconstruction of the (French) metallurgical industry. R. JORDAN. *Rev. métal.* 20, 493-516(1923).—An address on the reconstruction in the devastated regions of France. A. PAINNEAU-COUTURE

Status and recent progress of various metallurgies. MARCEL FOURMENT. *Rev. métal.* 20, 529-10(1923); cf. *C. A.* 17, 3009.—Brief review covering Sn, Sb, As, Hg, Bi, Cd, Cr, Mo, W, V. A. PAINNEAU-COUTURE

Antimony in 1922. F. C. SCHRADER. *U. S. Geol. Survey, Mineral Resources of U. S., 1922*, Pt. 1, 97-105(preprint No. 9, publ. Aug. 7, 1923). E. J. C.

The use of oxygen or oxygenated air in metallurgical and allied processes. F. W. DAVIS. *Bur. of Mines, Repts. Investigations No. 2502*, 2 pp.(1923).—A survey of O manuf. has shown that small demand has prevented large installations, and the greater part of the present cost represents the cost of transportation, storage, and service. Large plants can be built to deliver O at \$3 or less per long ton. Use of such O should cheapen furnace processes and make available large amts. of low-grade ores and fuels now considered worthless. A. BUTTS

Fuel oil aids cyaniding at the Belmont Shawmut. ANON. *Eng. Mining J.-Press* 116, 328(1923).—This mine on the Mother Lode, Calif., produces a pyritic Au ore, with dolomitic and calcareous gang. It was found that oil used in flotation aided subsequent cyaniding. Now flotation has been discarded and 8 to 10 lbs. of crude oil per ton of concentrates is added when regrinding for cyanide treatment. The new flow-sheet is given. A. BUTTS

The use of oxidizers in the cyanide treatment of concentrates. H. RUSHER AND J. HENDERSON. *J. Chem. Met. Mining Soc. S. Africa* 23, 231 9(1923).—At the Witwatersrand Cooperative Smelting Works, preliminary extn. tests are run on miscellaneous concentrates, which serve as reliable guides as to Au extn. and cyanide and lime consumption. In one trial 4.4 lbs. of $KMnO_4$ per ton of dry material was added, after amalgamation but before cyanidation—an amt. nearly enough to oxidize all the reducing matter in the ore. Extn. was thereby increased from 89 to 99%. Further tests with $KMnO_4$, PbO_2 , and BaO_2 generally gave improvement, but also gave some unexplained reversals. BaO_2 in an amt. of 0.75% of the dry ore gave the best results. *Cl. C. A.* 17, 1777. A. BUTTS

Recovery of gold absorbed in reduction works. A. KING. *J. Chem. Met. Soc. S. Africa* 23, 210-3(1923).—This article is not of a scientific nature but of interest because of its practical suggestions for the recovery of Au from deposits in or around reduction plants after a mine is finally shut down. Every part of plant, particularly the ground around the outside, underneath the stamp and tube mills, and plate house must be carefully examd. for Au. E. F. PERKINS

Silver recovery. G. F. PAUL. *Metal Ind.* 21, 364-5(1923).—A description of the recovery of Ag from moving picture lab. waste. E. J. C.

A resumé of copper leaching in Australia. H. R. SLEEMAN. *Eng. Mining J.-Press* 116, 193-6(1923).—A brief description is given of the processes of DuFaur, Corbould, Pechey, Smith, and Nevill-Soanes. These have been operated mostly on an exptl. scale. *Cl. C. A.* 16, 3054; 17, 373. A. BUTTS

Treatment of semi-oxidized copper ores. P. R. MIDDLETON. *Chem. Eng. Mining Review* 15, 314-6(1923).—The successful treatment of ores in which the Cu is present as both sulfide and oxide will open up enormous ore reserves. Both flotation and leach-

ing processes were tried but were unsuccessful because of high working costs. The most attractive process is the leaching with a suitable reagent and the pptn. of the Cu without sepg. the soln. from the solids, and then the recovery of both metal and sulfide as mixed concentrate in 1 operation. To ppt. the Cu, sponge Fe was found to be the most efficient and economical. This material is made by the reduction of magnetite without smelting or fluxing and cooling in an atm. free of O_2 to prevent reoxidation. This method gives a very porous and finely divided product. At the Chino Copper Company plant the following process is employed: After crushing and grinding the ore to a suitable mesh, it is agitated with a H_2SO_4 soln. until the ZnO is extd. The slightly acid pulp is nearly neutralized and then fed to the precipitator where sponge Fe is added to ppt. the dissolved Cu. The pulp then flows to a flotation machine which makes a concentrate contg. both Cu and CuS. Solvents other than H_2SO_4 that can be used are $FeCl_3$ or $Fe_2(SO_4)_3$. The $FeCl_3$ is an active solvent and can be readily and cheaply regenerated.

E. F. PERKINS

Blasting copper pigs. HINZ. *Z. ges. Schiess-Sprengstoffw.* **18**, 49-50 (1923).—Describes method of breaking up a pig of Cu weighing 10 tons, measuring $2.8 \times 1.2 \times 0.6$ m., which was practically a conglomerate containing 60-70% Cu together with layers of slag and chamotte from the furnace lining. Small charges of explosive are without effect on such material. A total of 55 kg. of "Silvit" in 16 charges of 3-4 kg. each were required to break up the pig in shape for remelting. All shots were "mud-capped." This method was considered more economical than drilled shots or the use of a saw on account of the toughness of the material.

C. G. STORM

Notes on the metallurgy of lead vanadates. WILL BAUGHMAN. *Trans. Am. Electrochem. Soc.* **43**, (preprint) (1923).—B. discusses the occurrence and concn. of lead vanadates in the U. S. The most satisfactory method of concn. is by gravity. Chloride volatilization applied to the Butte concentrates, the Baumann process for treating complex Pb-rare element ores, chloridizing roasting of the U. S. Vanadium Co.'s ores, Na_2S leaching of "Signal" ores, and the production of metallic V are discussed in turn. A flow sheet is given for Baumann's process, also one for the chloridizing plant of the U. S. Vanadium Development Co. The latter process has the disadvantages of unapplicability to ores containing large amounts of Ca and Mg and the requirement of large capacities for economic operation. Discussion of this paper brought out the fact that the metallurgy of lead vanadates has not been developed commercially because of lack of particular application of the metal rather than from the difficulty standpoint. Also leaching and treatment are too roundabout, with attendant high losses. Ferro-vanadium is best obtained in the elec. furnace. The use of Ti, or other N and O removers, and the better control in the case of elec. furnace steel, producing a steel in some way superior to V-steel, may diminish the demand for V.

W. H. ROYNTON

The practical results of the new theory of the blast furnace. W. MATHESIUS. *Stahl u. Eisen* **43**, 873-9, 907-12 (1923).—The carbon gasified in detrimental reactions in the blast furnace is expressed by $C_g = \frac{2}{3}O_s + C_{cs} = [n/(1+m)](C - C_F + C_{cs})$, in which C_g is the carbon gasified, C , the total carbon of the coke, C_{cs} , the carbon in the CO_2 of the ore and flux, C_F , the carbon in the pig iron, O_s , the oxygen of the ore, and m , the ratio by vol. of CO_2 to CO in the blast-furnace gas. The theory of the reactions taking place in the shaft of the furnace is discussed. The gases consist entirely of N, CO and H_2O . In the upper portions where the temps. are lower there is more CO_2 from the reduction of the ores and from the charge. The assumptions made in the calcs. were (1) that $\frac{1}{3}$ of the heat lost by radiation and cooling water was from the hearth area and $\frac{1}{3}$ from the shaft; (2) there is a difference of about 250° in the temp. of the gases as they pass into the shaft; (3) the temp. of the white iron in the shaft is 1400° ; (4) the entire sum of the heat was formed in the hearth. Curves are plotted from the data obtained and explained for the different furnaces considered and the ores used. From the curves, remedies can be suggested for highest recovery and use of coke. In the eupola, in the smelting zone the CO_2 formed is converted to CO in the glowing coke. This circumstance has a great influence on the direct reduction taking place in the shaft of the blast furnace. The actions of the upper Silesian and Westphalian cokes are discussed. The rate of reaction of the upper Silesian cokes in regard to conversion of CO_2 progresses as far as 850° as the Westphalian cokes do at 1000° . The consumption of the Upper Silesian coke in the furnace, per ton iron, is also larger than from good Rhenish Westphalian coke.

W. A. MUELLER

Malleable cast iron. ANON. *Bureau Bull. Brit. Cast Iron Research Assoc.* **1923**, No. 1, 10-4 (1923).—A bibliography.

E. J. C.

The iron and steel industry of Italy. G. E. FALCK. *J. Iron Steel Inst.* (London) (advance proof) **1923**, 22 pp.

E. J. C.

Producing steel castings. I. R. A. BULL. *Foundry* 51, 537-41(1923).—A general description of the steel casting industry in the U. S. and its development. II. *Ibid* 51, 571-4(1923).—The use of Mn, Si, and Al as deoxidizers is discussed. Acid elec. furnace development and practice, the question of S in scrap, and the design of furnaces are discussed in detail.

Characteristics of molding sands and their graphical representation. J. R. PERTCHER. *J. Iron Steel Inst.*, (advance proof) 18 pp.(1923).—The sand to be examd. is dried, passed through a 12-mesh sieve and then a $1\frac{1}{2} \times 9"$ test-tube is filled to a level 3" up from the bottom of the tube. The following tests are then made: (1) The sand is then covered with 4" of water, the vol. noted, the contents of the tube are shaken, and allowed to settle. (2) The tube is then filled to the brim with water, shaken, and allowed to settle, and the time taken for the fall of the sand grains (coarse, medium, and fine) until sedimentation is complete. (3) After the settling of the sand, the levels of silt, clay, and water are noted at definite time intervals until stable levels are reached. In expt. (1) the vol. represented by the fall of water level on shaking is a measure of the vol. of voids present; it is usually about 30-40%. The %, of voids is also a fair indication of the permeability of the sand to gases. In expt. (2) 3 generally distinct angles of slope occur, each corresponding with the velocity of the fall of the 3 different size grains in the sand. Curves made from such data very readily show the grain sizes present and also the relative proportions of the various sizes present. Different types of sands give different subsidence curves which are highly characteristic and furnish a way of satisfactorily comparing one sand with another. With sands contg. a relatively large % of silt and clay, a lag in the subsidence curve is always found. This fact is caused by the larger grains which in falling set up ascending water currents which are sufficient to prevent the descent of, and often actually carry up with them, the clay and silt. These small grains are carried up until their velocity becomes zero, then they begin their descent. These curves contg. such lags can be compared with standard curves and thus accurately interpreted. These curves are of great value in examg. the nature of "used" sands, and of mixts. of new and used sands with the purpose of detg. their fitness for use.

R. F. PERKINS

Correction to the freezing-point diagram of lead-sodium alloys. G. CALINGAERT AND W. J. BUESCH. *J. Am. Chem. Soc.* 45, 1901-4(1923).—The complete diagram of Pb-Na alloys is given for the following results: The pure compd. sepg. from alloys of Pb and Na, whose compn. is between 58.8 and 76.6 at. % Na, is Na_2Pb_3 , this compd. forming solid solns. with both NaPb and Na_2Pb . Alloys contg. 58.8 to 71.4 at. % Na rearrange at 182° on cooling; the compd. Na_2Pb_3 disappears and a new compd. Na_2Pb is formed.

JAMES M. BELL

Magnetic susceptibility and iron content of cast red brass. L. H. MARSHALL AND R. L. SANFORD. *Bur. Standards, Tech. Paper* 17, No. 221, 1-14(1922).—The magnetic characteristics of cast red brass contaminated with Fe are not a precise index of the Fe content, the magnetic susceptibility being markedly affected by changes in physical condition produced by heat treatment. Even after thorough annealing there is still no simple relationship between the magnetic susceptibility and Fe content. Less than 0.14% Fe goes into solid soln.; with greater amts. than this present an Fe-rich constituent appears as pale rounded areas. The Fe content has no noticeable effect on grain size.

S. L. CHISHOLM

Recrystallization of copper-zinc α solid solution. M. COOK. *Trans. Faraday Soc.* 17, 522-4(1922); *Science Abstracts* 25A, 635.—The results of expts. are given on the recrystn. and homogenization of unworked α brass contg. 70% Cu. The brass used was cast into $\frac{1}{8}$ -in. open iron molds, and the ingots thus obtained were annealed for different periods of time at different temps., and then examd. microscopically. When annealed for periods up to 7 hrs., at 400 to 500° , no perceptible change is noted in the original structure, the cored structure being very stable. When the annealing temp. reached 600° the change of structure became very marked with different periods of annealing, and specimens annealed at 650° for more than one hr. became completely homogenized.

H. G.

Typea of iron and steel which do not rust nor ignite. K. DARVES. *Praxis* 1, 270-1; *Physik. Ber.* 3, 667-8.—The difficulties encountered in working non-corrodible, high-Cr steels are lessened by reducing the C content and by corresponding heat treatment. Ordinary rust-proof steel consists of about 13% Cr, 0.5% Ni, and 0.7 to 1.0% C. After hardening it has a rigidity of 110 to 170 kg./mm.², which is not affected by heating to 500° . The coeff. of expansion is 11×10^{-6} . Both heat and elec. cond. are less than that for C steel. Cold work decreases resistance to rusting. Resistance to HCl and H_2SO_4 is not perfect but atm. oxidation does not take place even at 900° .

Where special hardness is not required a steel of 13% Cr and 0.1% C is recommended. These steels may be cast, forged, stamped, machined, etc. For surgical or dental instruments a higher Ni content is recommended. All these steels are useful for phys. or chem. app. used at high temps. Their cost is about 10-12 times that of ordinary steel.

A. E. STEARN

Non-residual steel. R. T. PIERCE AND T. D. VENSEN. *Elec. J.* 20, 160-1 (1923).—The development of a vacuum fused pure Fe-Si alloy, contg. less than 0.01% each of S and C, and possessing smaller residual magnetism than any previously known material, has made possible the construction of a new type of automobile ammeter which contains no coils, no springs, and no connections.

LOUIS JORDAN

Influence of thermal treatment on the capacity of hollow steel bodies. ALBERT PORTEVIN. *Rev. metal.* 20, 521-8 (1923).—From very large numbers of measurements carried out on shells of various calibers during the war the following conclusions are drawn: Increase in capacity on hardening increases with the temp. of hardening, is practically negligible below the transformation temp., increases with the hardness of the steel and with the energy expended in hardening, is practically unaffected by the length of time of quenching, and is cumulative with repeated hardenings. The rate and method of quenching (inside, outside, combined) have a considerable effect.

A. PAPINEAU-COUTURE

Some notes on the metals of the platinum group. F. E. CARTER. *Trans. Am. Electrochem. Soc.* 43 (preprint) 1923.—Some general remarks. All members of the Pt group are subject to gas absorption and the consequent difficulties of melting. The addn. of Ir to Pt raises considerably the temp. required for annealing. The phys. properties of each metal are given and alloys among the members of the Pt group are discussed.

W. H. BOYNTON

Action of mixtures of sulfuric and nitric acids on metals. P. PASCAL, GARNIER AND LABOURRASSE. *Mém. poudres* 20, 21-8 (1923).—Strips of Al, steel, and Pb were suspended in about 500 g. of the acid mixts. at 16-21° for periods varying from 1/2 to 24 hrs. and the rate of loss of wt. in g. per m.² per 24 hrs. was obtained. The results for a large number of mixts. of these acids, both dil. and concd., are given in a series of tables, and the lines of equal attack plotted on a series of ternary diagrams. These show clearly the range of concns. over which the metals are suitable for use in plants dealing with these acids. Al is not seriously attacked by H₂SO₄ over 98%, nor by HNO₃ at any strength, but is somewhat more vulnerable to mixts. of the acids. Steel plate is very little attacked by certain mixts. contg. less than 30% H₂O. The presence of NH₄NO₃ slightly increases the rate of attack of steel. Pure Pb resists mixts. of the 2 acids provided less than 30% H₂O is present.

J. S. C. I.

Norwegian As ores and As production (BUGGE, FOSLIE) 8. Recrystallization of metals and salts (TAMMANN, MANSURI) 2. Binary system, W-Mo (GEISS, VAN LIEMPT) 2. Relations of the potential surface of ternary alloys of Cd, Hg, and Sn or Pb (KREHMANN) 2. Refining Cu (Brit. pat. 193,894) 18.

Aluminium Facts and Figures. (Vest Pocket Edition). London: The British Aluminium Co., Ltd. 55 pp. 2s. 6d.

TAMMANN, GUSTAV: *Lehrbuch der Metallographie*. 3rd revised and enlarged ed. Leipzig: Leopold Voss. 450 pp.

Treating ores. MERRILL CO. Brit. 193,546, Dec. 5, 1921. Ores which contain constituents which interfere with the action of solvents or leaching agents such as cyanide are treated with an oleaginous substance unaffected by the solvent, with a view to destroying the action of the deleterious constituents. The ore is preferably ground in the presence of the oleaginous substance, which may be crude oil or coal tar, and the ore thus treated, without the removal of the deleterious constituents, is thereafter, with or without an intermediate drying, subjected to treatment with the solvent. In a modified method, the ore is ground with H₂O only and the oil, etc., is mixed with the pulp subsequently.

Treating ores. Z. METZL. Brit. 195,556, June 16, 1922. Au and Ag ores contg. Sb are treated at 70 to 100° in the presence of quicklime with a very dil. soln. of Na₂CO₃ or other alk. carbonate; air is admitted and the mixt. agitated. The precious metals are left undissolved, and thioantimonates and other salts are formed which may be decomposed by CO₂, e. g., in the form of smoke, Sb sulfide being pptd.

Concentrating ores. EUREKA METALLURGICAL CO. Brit. 194,260, Nov. 21, 1922. A flotation process of coneg. ores, particularly oxidized or non-sulfide ores, consists in

intimately mixing addn. agents, which assist the subsequent flotation action, before introducing them into the pulp of the ore. A pulverized alk. sulfide, such as Na_2S , is made into a paste with a melted hydrocarbon such as paraffin, the mixt. being stirred while solidifying. This mixt. is then broken into fragments and introduced into a tube mill together with the ore to be ground into a pulp, or it may be introduced into the pulp after the ore has been ground and passed into an emulsifier. Another method of mixing consists in grinding the two ingredients together and heating to such a temp. that the Na_2S is not fused and then spraying the mixt. into the pulp. The mixt. will not produce a froth and therefore oils such as pine oils are added to expedite the formation of a froth in the flotation cell.

Reducing ores. L. P. BASSET. Brit. 191,280, Feb. 16, 1923. In the reduction of ores, and particularly iron ores, the ores are mixed with the quantity of coal necessary for their reduction and with suitable fluxes and the mixt. is subjected to the action of a flame obtained by the combustion of pulverized coal in the necessary quantity of superheated air which produces CO and CO_2 , the latter in the smaller quantity so that the flame can never exert a prejudicial oxidizing action on the metal. Cf. 132,262, 110,096, and 158,523 (C. A. 15, 1877).

Classifying ores, etc. R. H. SMYTH. Brit. 195,113, Sept. 11, 1922. In the classification of ores, clays, etc., according to wt. prior to concn. by flotation or by means of bubbles, vanners, or other sepg. plant, the materials mixed with H_2O are caused to flow through launders into which a mineral salt such as Al or Mg sulfate, and hydroxide of Ca or NH_4 are introduced. The insol. gelatinous Al or Mg hydroxide so formed binds together the finer particles and the stream is then caused to enter the first of a series of settling tanks. The heaviest particles sink in the first tank and the overflow passes successively into the remaining tanks in which the particles sink according to wt. A dil. acid such as H_2SO_4 , HCl , HNO_3 , or HOAc is then added to each of the tanks. This dissolves out the excess hydroxides and liberates the particles in such a condition that they can be easily concd., the contents of each tank being treated separately.

Enriching purple ore. O. W. BOKELUND. Swed. 52,639, Sept. 6, 1922. The purple ore is heated with coal or other reducing agents in the absence of air. The magnetic Fe compds. formed are sepd. magnetically.

Briquets from slimy ores. AKTIEBOLAGET ELEKTROLYTVERKEN. Swed. 50,581, Jan. 4, 1922. The slime is mixed with purple ore and similar products contg. water-sol. binding substances and with finely ground coke or charcoal and water, and is then pressed to briquets and dried.

Extracting metals. H. S. MACKAY. Brit. 191,353, Nov. 11, 1921. Pb is extd. from ores by first converting it to sulfate, leaching the product with a chloride soln., and continuously pptg. the Pb from the resulting soln. on a metal such as Fe. The process may be combined with the recovery, in successive stages, of the various metals contained in complex ores. In a process for the treatment of sulfide ores contg. Cu, Zn, Pb, Ag, and Au, the ores are crushed, roasted, and leached with H_2SO_4 to recover Cu and Zn, the soln. of these metals being electrolyzed or otherwise treated for the recovery of the metals. The residues after the removal of the Cu and Zn are treated with hot NaCl soln., the soln. of PbCl_2 being continuously drawn off and pptd. on Fe or other metal preferably in the form of dust. The FeCl_2 soln. formed is used with or without NaCl as a solvent for further PbSO_4 . The residues from the extn. of the Pb are treated with cyanide for the extn. of Au and Ag, the metals being pptd. from the cyanide soln. on Zn dust. Ag may be recovered along with the Pb by roasting the ore so as to convert both the Pb and Ag to sulfates, leaching with chloride, and pptg. with Fe. The extn. of the Zn and Cu from the complex ores may be effected as described in 26,138, 1913.

Extraction of mercury. M. K. COMBING. Can. 233,792, Aug. 28, 1923. Hg is extd. from sulfide ores by agitating the finely divided ore with a saline soln. (NaNO_3 and Na_2CO_3) in the absence of reducing metals and the Hg thus sepd. is recovered by means of preformed Hg through which the mixt. of soln. and ore may be passed. The latter step may be repeated as often as necessary. Cf. C. A. 16, 895.

Making porous metals. K. KATSUMORI. Brit. 191,455, Nov. 12, 1921. Porous metals, suitable for electrodes, are made by heating an alloy of Ni and Mg, or Ni, Mg and Co, to a temp. above that at which the eutectics melt, and subjecting the heated alloy to treatment in a centrifugal separator whereby the eutectics are removed, leaving a porous metal. An alloy consisting of 97% of Ni and 3% of Mg is heated to 1300° and treated by the above process. A eutectic consisting of 89% of Ni and 11% of Mg is driven off, leaving porous Ni. In another example, an alloy is used which consists of 97% of Ni, 2.8% of Mg, and 2% of Co, heated to a temp. of 1100 – 1300° . The alloy may be in the form of a plate, rod, etc., and the resulting porous metal may be used

in the condition in which it is obtained or it may be set in a frame and used as a battery electrode. Porous nictals so obtained may also be used as electrodes in the elec. decomn. of H_2O .

Enriching roasting gas with sulfur dioxide in roasting sulfidic ores which are deficient in sulfur. HUGO PETERSEN. Ger. 310,073, Aug. 26, 1920. The process is adapted to such ores as zinc blende. Air is used in as small excess as possible along with the fuel gas. The gas and air enter the oven by numerous openings out of which the ore falls when roasted, the fuel gas entering in a tangential direction. The draft for the fuel gas and air is independent of the draft in the roasting oven. Air is also admitted to stirring arms in order to cool them, the admission being controlled by means of slides.

Sulfuric acid from blast treatment of copper mat. METALLBANK UND METALLURGISCHE GESELLSCHAFT AKT.-GES. Ger. 310,621, Aug. 20, 1920. Cu mat in molten condition is conducted in an uninterrupted stream to the blast chamber which is provided with means for catching and conducting off the SO_2 produced in the blast operation. The slag and the Cu mat which have been subjected to the blast flow away likewise in continuous stream.

Treatment of blast-furnace slag. HUGO PETERSEN. Ger. 309,134, Oct. 25, 1919. Slag flowing from different blast furnaces is first collected in a well insulated container and from this amt. is taken for air treatment in smaller containers.

Metallurgical furnaces. B. B. FOGLER. Can. 233,855, Aug. 28, 1923. Structural features are specified of an app. for converting an ore into a sol. compd. of the desired metal and for placing the compd. in soln.

Fluxes. A. PASSALACQUA. Brit. 194,729, March 13, 1923. An agent for prep. the surface of metals, particularly Al and its alloys, for tin-plating consists of a mixt. of 4 compns., the first comprising stearic acid, paraffin, resin, linsed oil, olive oil or similar oil, and lard, or similar fatty substances, the second comprising $SnCl_4$, $Al_2(SO_4)_3$, $AlCl_3$, Na pyrophosphate, sal-ammoniac, NaOH soln., tin sulfate, HNO_3 , $ZnCl_2$ and H_2O , the third comprising $NiSO_4$, NH_4Cl , citric acid and distd. water, and the fourth comprising $SnCl_4$, Na pyrophosphate and distd. water. In prep. the compn. a mixt. of the last 3 solns. is added to the first mixt. and the whole is brought to boiling. The compn. is applied to one face only of the slightly heated metal, which is then subjected to a temp. of about $425-50^\circ$. Tin is applied by means of a metallic brush which also removes dross.

Iron and steel. L. P. BASSET. Can. 234,361, Sept. 18, 1923. In the direct production and refining of Fe and steel the ore is incompletely reduced and the unreduced portion assists a basic slag in preventing the reduction of phosphates, silicates, etc. The furnace is heated with pulverized fuel and superheated air burned to produce only CO . Cf. C. A. 16, 2671.

Desulfurizing steel, etc. J. T. PRATT, D. D. JACKSON and J. D. SEARS. Brit. 193,851, Feb. 22, 1923. In a process for desulfurizing Fe, steel, iron alloys and Cu, the molten metal is treated with a mixt. of an alkali silicate and either an alk. hydroxide or carbonate or both, the Na compds. preferably being used. The silicate may form 5-15% of the mixt. The mixt. is spread out as a liquid layer on the molten metal in a ladle crucible, converter, etc., the slag having been removed, or is fused to form a block which may be coated with paraffin wax.

Alloys. F. FINCH and J. JACKSON, Lth. Brit. 195,189, Jan. 11, 1922. A Cu-Sn-Al alloy, which may contain, e. g., Cu 8.95, Sn 4.47 and Al 86.58%, or Cu 10.5, Sn 5.5, and Al 84%, is made by melting the Cu and an equal wt. of Al with the aid of a flux of $MgCl_2$ and borax; the alloy so formed is then melted with the Sn and the remainder of the Al, a flux being used as before.

Alloys. ALUMINUM CO. OF AMERICA. Brit. 195,048, Feb. 14, 1923. Sb or Bi is added to Al alloys contg. a substantial proportion of Si. The Si-Al alloy, which may contain 3 to 15% of Si, may be prep. by stirring Si into molten Al at 750 to 800° . The Sb or Bi, preferably 0.5 to 1.5%, is preferably added to the molten alloy in pulverized form. The Fe content should preferably not exceed 0.6%, but may reach 1.5%. Cu or Zn may also be present. The molten alloy is preferably cooled quickly, as by chill casting. Cf. C. A. 17, 1068, 1069.

Alloy metal powder. W. P. HESKETT. Can. 233,908, Aug. 28, 1923. An alloy in the form of a self disintegrating powder is produced by combining the metals at their respective m. ps. e. g., Mn 40, Fe 19, Cu 10, Al 10, Sn 5, Zn 15 and Pb 10% may be so alloyed and on cooling the product will disintegrate into a fine powder.

Alloy powders. J. SEJOURNET. Brit. 195,064, March 12, 1923. Equal amts. of Mg and Al are melted together, preferably in a graphite crucible in an elec. furnace, and in the presence of an inert gas or a reducing agent. The molten charge is stirred

to obtain the alloys Al Mg, Al₃Mg₄ which on cooling are crushed to a fine, homogeneous powder which may be used in the prepn. of flash-light compos., fireworks, explosives and thermo-aluminic mixts. Either of the alloys may be separately prepd. and crushed and the powders used together.

Acid-proof alloy. H. TERRISSER and M. LEVY. Can. 234,358, Sept. 18, 1923. An acid-proof alloy contains Fe 50-88, Si 30-10 and W 20-2%.

Coating aluminium. ALUMINUM CO. OF AMERICA. Brit. 195,625, March 23, 1923. Al is alloyed with at least 4% of Si, and the alloy is treated so as to form on its surface a layer of Si which resists corrosion, forms a basis for paint, electroplating depositions, etc., and also serves as a self-lubricating bearing material. In the treating process which is termed "silurizing," the alloy is pickled in either acid or alkali solns. or both, and then subjected to the action of aqua NH₃ at about 50-80°. If the articles are free from grease the pickling may be omitted. Articles to be electroplated need not be treated with NH₃.

Cementation of boron into iron, etc. T. MIYAGUCHI. Brit. 193,918, Nov. 3, 1921. A hard and tough surface layer is obtained in Fe and steel alloys by a cementation process in which the Fe, etc., is heated to a temp. of 800-900° in contact with powd. ferro-boron or a mixt. of B oxide or other B compd. and C powder in the presence of a continuous stream of Cl gas. Parts of the surface not required to be affected are protected by an Fe plate, Fe powder or clay.

Cementation of boron into iron, etc. T. MIYAGUCHI. Brit. 193,917, Nov. 3, 1921. A hard and tough surface layer is obtained in Fe and steel or steel alloys by a cementation process in which the Fe, etc., is heated to a temp. of 800° to 900° in contact with C powder and B oxide or other B compd. such as borax, or ferro-boron in a reducing atm. such as a gas contg. CO. Parts of the surface not required to be affected are protected with clay. Cf. 19,461, 1912 (C. A. 8, 187) and 193,918 (above).

Making tools and other hard, tough, shaped objects. GENERAL ELECTRIC CO., LTD. Brit. 195,093, March 19, 1923. Dies for drawing W, Mo or other wire, gages, tools for metal working, and other objects are made from W or Mo or other carbides of high m. p. soaked in Fe or other metal. The carbide or mixt. of metal and C may be pressed into the desired form and sintered or a metal form may be carbonized by treating with tar, sugar soln., etc., or packing in C dust or placing in an atm. of coal gas, CO, etc., and then heating. The carbide form is then immersed in molten Fe or sheet Fe may be placed on the largest surface and melted, the other surfaces being then similarly treated.

Welding cast iron by the electric arc. M. LEBRUN. Can. 233,880, Aug. 28, 1923. The elec. current is caused to flow through a gray cast iron electrode while C is added to the weld.

Electrodes for arc-welding, etc. W. H. BOORNE. Brit. 193,585, Dec. 20, 1921. Electrodes for arc-welding and metal cutting are provided with a covering of which green fibrous asbestos, known as actinolite, is a constituent in a yarn like pulverized or other form. The actinolite may be wound round a metal electrode and applied together with a soln. of Na₂SiO₃ and powd. Al or Mg. Alternatively the actinolite may be powdered and mixed with Na₂SiO₃. Graphite, magnesite, and powd. Al or Mg may be added to the mixt. Any other suitable materials may be used to form the flux so as to strengthen or counteract any properties of the actinolite. Cf. 132,354 and 157,509 and C. A. 17, 970.

10—ORGANIC CHEMISTRY

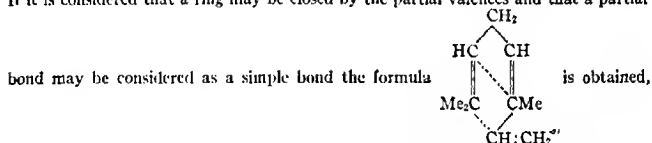
CHAS. A. ROUILLER AND CLARENCE J. WEST

Addition of hydrogen to acetylene derivatives. VIII. Y. S. ZAL'KIND. *J. Russ. Phys. Chem. Soc.* 43, 1830-48 (1916).—When β,ϵ -dimethylhexine- β,ϵ -diol is reduced with H by the Sabatier process, with a Pd catalyst, two stereoisomeric ethylenic reduction products may be obtained, namely, the *cis*- and *trans*-isomerides of β,ϵ -dimethyl- Δ^7 -hexene- β,ϵ -diol, $\text{HOCMe}_2\text{CH:CHCMe}_2\text{OH}$. One isomeride, the α -form, m. 76.5-77°, while the β -isomeride m. 69-9.5°. The dehydration of these substances by H_2SO_4 leads to the production of 2,3-dihydro- β -xylene: $\text{HOCMe}_2\text{CH:CHCMe}_2\text{OH} \rightarrow \text{CH}_2\text{:CMeCH:CHCMe}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CMe:CHCH:CMc}$. The two isomerides

are not interconvertible under the conditions of the catalytic reduction, but are formed side by side, the quantity of each isomeride in the reaction product being detd. by the velocity with which the reduction is conducted. Thus if a large quantity of catalyst is

used, the reduction proceeds rapidly to completion, giving as the main product the α -isomeride, while a slow reduction produces principally the β -form. Both isomerides are converted by heat or by mild dehydrating agents into the γ -lactone, the α -form suffering dehydration more readily. With PBr_3 , they give an oily, unsatd. monobromide, $C_8H_{13}Br$. Bromination of the isomerides gives for each an oil and a cryst. compd., m. 98.5-9.5°, both having the formula $C_8H_{10}O_2Br_2$. From the α -isomeride, the main product is the oil, which is obtained as a by-product from the bromination of the 2nd form. It is probable that some conversion of the stereoisomerides is effected in each case by the HBr liberated during bromination. J. C. S.

1,3,5-Heptatriene and some related substances. C. J. ENKLAAR. *Rec. trav. chim.* 42, 524-7 (1923).—Previous work on the synthesis of unsatd. hydrocarbons (*C. A.* 7, 1169) led E. to synthesize 1,3,5 heptatriene (I) (*C. A.* 7, 1704). The refractive and dispersive powers of I were found to be the mean of those of phenylbutadiene and of phenylpentadiene. The values for these consts. for I are lower than those required by v. Auwers and Eisenlohr's theory. In certain cases v. A. and E. attributed the abnormal values to a polymerization and E. has shown this interpretation to be of some value with I as indicated by the fact that d_4^{17} changes from 0.7550 to 0.765 in 6 months. It is also shown that the normal values as calcd. by v. A. and E. require a small correction. E. suggests that the stereoisomers of heptatriene and hexatriene prep'd. by means of $KHSO_4$ are stable in the presence of acid while the hexatriene obtained from the bromide by means of Zn ought to be the unstable form. The I is exclusively the *ac*-form. If allocimene (III) is considered to be formed by the displacement of a double bond in ocimene, $H_2C:CMcCH_2CH_2CH:CMcCH:CH_2$, then III may be $Me_3C:CHCH_2CH:CMcCH:CH_2$. If it is considered that a ring may be closed by the partial valences and that a partial



i. e., a trienic system. The above considerations are of importance in indicating directions in which the practical investigation may be extended. E. J. WITZEMANN

Commercial syntheses starting from acetylene. A. GUYOT. *Chimie et industrie* 10, 13-22 (1923).—A review covering the prep'n. of $CH_3CH_2CHCl_2$, $CHCl:CCl_2$, $CH_2Cl:CO_2H$, $CHCl:CHCl$, C_2HCl_3 , $CCl_2:CCl_2$, C_2Cl_4 , $CH_2:CHCl$, C_2H_4O , $(C_2H_4O)_n$, $(C_2H_5O)_n$, $AcOH$ and $EtOH$. A. PAPINEAU-COUTURE

Tertiary methylheptanols. II. The catalytic hydrogenation of tertiary unsaturated methylheptyl alcohols. V. GRIGNARD AND R. ESCOURROU. *Compt. rend.* 177, 93-6 (1923); cf. *C. A.* 17, 3137. —The satn. of the double bond was carried out by 2 methods, the first using Pt as the catalyst, and the second using Ni. In the first case the H_2 was led in at the beginning of the expt. under a pressure of 1 m. of water. By carrying the pressure to 0.5 atm. the rate of hydrogenation was noticeably increased. The hydrogenation proceeded regularly for the 1st members of the series, but in the case of the Pr and Bu derivs. the reaction was hindered by the formation of propane and butane, by ketonic decompn., which prevented the entrance of the H_2 . Hydrogenation proceeded when the atm. was renewed, but a different alc. was obtained than would have been if no decompn. had taken place. When the hydrogenation of ethylmethylheptenol was carried out in the presence of Ni at 300° by the method of Sabatier and Senderens, and that of dimethylheptenol at 180°, the O was completely removed, and the olefin was hydrogenated. This was overcome by reducing the pressure. Dimethylheptenol was completely transformed into 2,6-dimethyl-6-heptanol under 14 mm., at 160-70°. No ketonic decompn. took place, and the rate of hydrogenation was not decreased. The explanation is given that at higher pressures both alc. and H_2 are absorbed by the catalyst, while at lower pressures the H_2 only is absorbed. The removal of the O is due to the double bond, as the satd. alc. may be passed over Ni at atm. pressure and 180° without this reaction's taking place. A table of the properties of the methylheptanols and their corresponding satd. compds. is given. R. G. FRANKLIN

Preparation of organo-magnesium compounds without the use of ether. P. NGOGI. *Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, cxxxi (1921). —Cheluzev prep'd. organo-Mg compds. without ether by using tertiary amines as catalysts, the amines forming at first tetra-alkyl or-aryl compds. which react with Mg to form or-

gano Mg compds. liberating the free amines. It has been shown that these compds. may also be prepd. in neutral solvents by the use of trialkylsulfonium iodides as catalysts. *E. g.*, by using minute quantities of Et_3SI , organo-Mg compds. have been obtained with Me, Et, Pr, iso-Bu and iso-Am iodides, the reaction being analogous to that observed in the case of tertiary amines.

H. G.

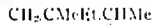
A new way from carbon dioxide to formaldehyde. T. THUNBERG. *Svensk Kem. Tids.* 35, 145-50 (1923).—5 g. PbCO_3 , 60 cc. redistd. H_2O , 30 cc. 3% H_2BO_3 and 10 cc. Merck's perhydrol, were placed in a 250 cc. Kjeldahl flask which was provided with a 3-bulb distg. tube and 50 cc. distd. The distillate gave positive tests for HCHO with the Schiff, Rimini-Schriver, and Demigès-Grosse-Rohle reagents. The heating of this reaction on the newer conceptions of plant respiration is discussed in detail. (Cf. Wieland, *Ergebn. Physiol.* 20, 477; Kleinstück, *C. A.* 12, 1721; Wislizenus, *C. A.* 13, 1483.)

A. R. ROSE

Condensation products of methyl ethyl ketone. J. B. EKELEY AND W. W. HOWE. *J. Am. Chem. Soc.* 45, 1917-25 (1923).—Only 1 compd. corresponding to a *homomesityl oxide* occurs among the condensation products obtained from MeCOEt with H_2SO_4 or NaOEt and with KMnO_4 ; it gives only EtCOEt ; it must therefore have the structure CMeEt:CHCOEt (I). Three other condensation products have the comp. $\text{C}_{10}\text{H}_{18}\text{O}$; 2 of these are identical with compds. obtained by condensing I with AcCH_3 , CO_2Me and must therefore be the *homoisophorones* (II and III). The non occurrence of the theoretically possible isomer CMeEt:CMCOMe of I shows that it must have been used up during the reaction to form homophorones by condensing with another mol. of MeCOEt . The exaltation of the mol. refraction of the 3rd compd. $\text{C}_{12}\text{H}_{20}\text{O}$ (IV), its b. p. (next highest to I in the series of condensation products of MeCOEt) and the fact that MeCOEt with HCl yields only I and IV indicate, from analogy with the Me_2CO condensation products, that IV is a *homophorone*. I, oil of a peppermint like odor and camphor like taste, $b_{45} 156-60^\circ$, $d_4^{20} 0.8628$, $n_D^{20} 1.4453$, mol. wt. (vapor d. method) 131.2; *avime*, $b_1 132-7^\circ$; with 1 mol. $\text{H}_2\text{NCONHNH}_2$ in alc. is obtained a cryst. pld., m. 114.5° (cf. Bodroux and Taboury, *C. A.* 4, 1937), but it is a mixt. sepd. by means of H_2O EtOH into fractions m. 149° and 108° ; with 2 mols. $\text{H}_2\text{NCONHNH}_2$, HCl in alc. is obtained the *semicarbazide semicarbazone*, $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}$, m. 265.6° (decomp.). IV, slightly straw-colored liquid of camphor-like odor and taste, $b_{45} 206-10^\circ$, $d_4^{20} 0.8857$, $n_D^{20} 1.4792$, mol. wt. 172-85. II and III: *Cy* isomer, clear yellow liquid of weak terpene taste and odor, $b_{45} 256-60^\circ$, $d_4^{20} 0.9492$, $n_D^{20} 1.5015$, mol. wt. 178.88, gives with dry HCl in CS_2 a heavy black oil, hydrolysis of which with standard NaOH indicates the presence of only 1 double bond in the original compd.; the other isomer, golden brown, slightly viscous liquid of camphor-like odor and taste, $b_{45} 280.5^\circ$, $d_4^{20} 0.9933$, $n_D^{20} 1.5115$, mol. wt. 168-79.



II



III

C. A. R.

The ketenic decomposition of methyl ethyl ketone. C. DEW HURD AND CYRIL KOCOUR. *J. Am. Chem. Soc.* 45, 2167-71 (1923); cf. *C. A.* 17, 1427. It was shown in the earlier paper that $\text{CH}_2\text{:CO}$ can be obtained by heating Me_2CO vapors in a suitable app. (by using tightly fitting rubber stoppers in place of corks wherever possible and, where corks were used, by softening them well and painting them with water glass inside and outside 1 day before use, the yield of purified AcNHPh , based on the amt. of unrecovered Me_2CO , was increased from 17.5 to 28.3%; the true temp. of the furnace was probably somewhat higher than the 600° reported in the 1st paper). MeCOEt similarly treated also gives $\text{CH}_2\text{:CO}$ but no MeCH:CO was detected, although it may have been formed and then decompd. at the high temp. of the expt. Condensation products of MeCOEt constituted 4-5% of the distillate, the other 95%, consisting of unchanged MeCOEt . As $\text{CH}_2\text{:CO}$ and MeCH:CO are gases that easily polymerize, no attempt was made to isolate them but instead, reagents were sought that would differentiate between them (PhNH_2 , $p\text{-MeC}_6\text{H}_4\text{NH}_2$, H_2O). The yield of ketene, based upon the unrecovered MeCOEt , was 1-3.5%.

C. A. R.

Direct conversion of derivatives of dichloroacetic acid into derivatives of trichloroacetic acid. A. S. WHEELER AND S. C. SMITH. *J. Am. Chem. Soc.* 45, 1934-8 (1923); cf. *C. A.* 17, 3324.—It was shown in the earlier paper that the nitroamines treated with $\text{CHCl}_3\text{CO}_2\text{H}$ and P_2O_5 give nitrodichloroacetamides. Aromatic amines in the absence of a dehydrating agent behave differently. When brought together with 1 mol. of $\text{CHCl}_3\text{CO}_2\text{H}$ at 0° or a lower temp., they yield a simple amine salt of $\text{CHCl}_3\text{CO}_2\text{H}$

but when an excess of acid is used and the heat of the reaction is allowed to take its course, a complex reaction takes place, the product being a deriv. of $\text{CCl}_3\text{CO}_2\text{H}$ of the structure $\text{CCl}_3\text{CO}_2\text{NH}_2$ or $\text{CCl}_3\text{C}(\text{OH})_2\text{NHR}$; the $\text{CCl}_3\text{CO}_2\text{H}$ is probably formed according to the scheme $2\text{CHCl}_2\text{CO}_2\text{H} \longrightarrow \text{CCl}_3\text{CO}_2\text{H} + \text{CH}_2\text{ClCO}_2\text{H}$ under the influence of the base. *o*-Toluidine dichloroacetate (8.5 g. from 5 g. of the amine and 6.1 g. of the acid in cold CCl_4), m. 140° , becomes brown in the air and light, changes into the $\text{CCl}_3\text{CO}_2\text{H}$ salt on long boiling with H_2O ; *p*-isomer, m. 160° . Aniline trichloroacetate (7.5 g. from 5 g. PhNH_2 and 7 cc. $\text{CHCl}_2\text{CO}_2\text{H}$, H_2O being added and heat applied until the product dissolves), m. 163° , becomes reddish in the air, decompd. by KOH with liberation of PhNH_2 and by H_2SO_4 with formation of $\text{CCl}_3\text{CO}_2\text{H}$, is identical with the product obtained from PhNH_2 and $\text{CCl}_3\text{CO}_2\text{H}$ gently heated together or mixed in CCl_4 at -3° . *o*-Toluidine trichloroacetate, m. $167-8^\circ$ (decompn.), forming CHCl_2 and CO_2 . *p*-Isomer, m. 135° (decompn.). α -Naphthylamine trichloroacetate, pale violet, m. 173° (decompn.). *m*-Nitroaniline salt, pale yellow, m. 147° . When 5 g. p - $\text{O}_2\text{N}-\text{C}_6\text{H}_4\text{NH}_2$ was warmed with 12 cc. $\text{CHCl}_2\text{CO}_2\text{H}$, then heated 10 min. on the H_2O bath with P_2O_5 , poured into cold H_2O and allowed to stand overnight and the ppt. was extd. with CCl_4 , there remained undissolved *p*-nitrochloroacetanilide, yellow, m. 177° , and the CCl_4 ext. yielded the trichloroacetanilide, light yellow, m. 140° . C. A. R.

A gallotannin apparently free from glucose. M. NIERENSTEIN. *Analyst* **48**, 321-2 (1923).—Contrary to the theory that gallotannin is galloylglucose, Mitchell found by a colorimetric method (cf. *C. A.* **17**, 1401) that gallotannin yielded almost no glucose on hydrolysis. Acid hydrolysis by the method of Fischer and Freudenberg (*C. A.* **6**, 2428), by that of Feist and Haun (cf. *C. A.* **8**, 1219), and with tannase from *Aspergillus luchuensis* and detn. of the products polarimetrically and by the reduction method of Bertrand (cf. *Bull. soc. chim.* **35**, 1285 (1906)) gave in no case over 0.6% glucose by the polarimetric or 1.2% by the reduction method and thus confirmed the results of M. The latter method is unreliable because gallic acid gives a product which reduces Fehling soln. (cf. Baker and Strutt, *C. A.* **8**, 2283). Also in *J. Soc. Leather Trades' Chemists* **7**, 317-8 (1923). C. C. DAVIS

Characteristics of the two crystalline forms of glycine. C. A. BRAUTLECHT AND N. F. EBERMAN. *J. Am. Chem. Soc.* **45**, 1934-41 (1923).—The 2 forms were pulverized, sifted and dried at $100-3^\circ$. Photomicrographs before pulverization indicated that the plate form at times contained occluded H_2O which was apparently removed by the pulverizing, drying and sifting to 0.3 mm. mesh. So prepa., both forms decompd. at the same temp. (233°). Ground uniformly in dried air, both forms lost the same amt. in wt. at 100° (0.28-0.31%). With dry HCl in a bell jar contg. a tray of CaCl_2 the 2 forms increase in wt. in 6 days by amts. corresponding to the formation of 70-100% of glycine-HCl (1); if the CaCl_2 is replaced by a dish of H_2O , the amt. of 1 formed in 6 days from either form is uniformly 90-100%. With SO_2 in a bell jar under ordinary moisture, temp. and pressure conditions the increase in wt. of the needle form in 6 days corresponds to about 98% diglycine sulfite formation, that of the plate form to 87-95.5%; with dry SO_2 and powdered crystals there is practically no absorption (less than 1 part per 100 with the needle and none at all with the plate form). The dry powdered crystals do not add enough Br even after 6 days to form the monobromide (av., 67%), the needles, however, reacting somewhat more readily than the plates; under atm. moisture conditions, the results are irregular, sometimes the 1 form, sometimes the other adding more Br than the amt. calcd. for the dibromide; with moist Br enough is taken up by both forms in 45 min. to give 67% of the monobromide; after 5 hrs. is obtained a dark red liquid from which colorless glycine is recovered on drying. With AcCl and PCl_5 both forms (which had been allowed to stand after pulverization) yielded about 10% $\text{ClH}_2\text{NCH}_2\text{COC}(\text{Cl})_2$ (II), while 10 g. of the fresh needles gave 8.5 g. II and 10 g. of the plates yielded 3 g. of what was apparently $\text{ClH}_2\text{NCH}_2\text{CO}_2\text{H}$. PCl_5 or PCl_3 alone in CS_2 have no action on either form. Neither form reacts with EtI in boiling abs. alc. after 2 days. C. A. R.

The industrial manufacture of urea. PAUL BAUD. *La Nature* No. 2551, 116-8 (1923).—A discussion of the process of Matignon and Fréjacques, by which CO_2 and NH_3 form $\text{NH}_4\text{OCONH}_2$; this splits off H_2O giving $(\text{NH}_2)_2\text{CO}$. A diagram is given of Fréjacques' continuous app. JACK J. HINMAN, JR.

Additive reactions of thiocyanogen. H. P. KAUFMANN. *Ber. pharm. Ges.* **33**, 139-48 (1923).—Solns. of $(\text{SCN})_2$ or the substance in nascent condition were applied in suitable media in the prepn. of ethylene dithiocyanate, $\text{C}_2\text{H}_4(\text{SCN})_2$, m. 90° ; styrene dithiocyanate, $\text{C}_8\text{H}_8(\text{SCN})_2$, m. $101-2^\circ$; allyl alc. dithiocyanate, $\text{C}_3\text{H}_7\text{OH}(\text{SCN})_2$, an oil decomp. on distn.; anethole dithiocyanate, $\text{C}_{10}\text{H}_{16}\text{O}(\text{SCN})_2$, m. 87° ; isosafrole dithiocyanate, $\text{C}_{10}\text{H}_{16}\text{O}_2(\text{SCN})_2$, m. 109° . An attempt to prep. the thiocyanate of

$\text{AcCH}_2\text{CO}_2\text{Et}$ finally led to the formation of $\text{Et } m\text{-hydroxymethylthiazolecarboxylate}$, $\text{C}_7\text{H}_9\text{O}_2\text{SN}$, $m. 128^\circ$. β -Naphthol gave with $(\text{SCN})_2$ in $\text{C}_6\text{H}_5\text{Cl}$ β -naphthol γ -thiocyanate, $\text{C}_{10}\text{H}_7\text{OSN}$, $m. 68-70^\circ$, which on reduction is changed to the mercaptan, $\text{C}_{10}\text{H}_7\text{OS}$, $m. 106^\circ$, as shown by the latter's conversion into the 2,2'-naphthol 1,1'-disulfide, $\text{C}_{10}\text{H}_6\text{O}_2\text{S}_2$, $m. 165^\circ$. With $\beta\text{-C}_6\text{H}_4\text{-OCH}_3$, $(\text{SCN})_2$ unites to form the thiocyanate, $\text{C}_{12}\text{H}_9\text{OSN}$, $m. 134^\circ$, which in turn is reduced to the mercaptan, $\text{C}_{12}\text{H}_9\text{OS}$, $m. 98^\circ$. Similarly, α -naphthol gives the compd., $\text{C}_{10}\text{H}_7\text{OSN}$, $m. 85-7^\circ$, the latter in turn the mercaptan, $m. 113^\circ$ and disulfide, $m. 152^\circ$. The expts. show that free $(\text{SCN})_2$ unites with unsatd. compds. but with less energy than Br, occupying in this respect a position between Br and I.

W. O. E.

Resolution of the α , β -dihydroxy- α -methyl- β -isopropyladipic acids. T. A. HENRY AND HUMPHREY PAGET. *J. Chem. Soc.* 123, 1878-87 (1923).—It has been shown (C. A. 16, 612) that α -terpinene from chenopodium oil on oxidation with KMnO_4 yields two α , β -dihydroxy- α -methyl- β -isopropyladipic acids, $m. 189^\circ$ (I) and $203-4^\circ$ (II), the yield from 1000 g. α -terpinene being about 10 g. I and 5 g. II. Wallach (C. A. 2, 3332) has synthesized I from $\text{AcCH}_2\text{CH}(\text{COCH}_3)\text{Me}$, but in repeating his work it has been found that I and II as well as a new isomer (III), $m. 198^\circ$, are formed in the ratio 1:3:1; the methods of sepn. are given. II, boiled with HCl , does not lose 2 mols. of H_2O , as Wallach stated, but does so when dry distd.; the supposed "dilactone" is really the anhydride of 1,4-cineolic acid (Nelson, C. A. 5, 3396). This establishes II as the *anti*-acid. I, when boiled with HCl , yields a lactone, $m. 74^\circ$, in 50% yield, the remainder of the acid having been converted into II. The lactone, on hydration, yields III, which reproduces the lactone on boiling with HCl . I is really a mixt. of II and III, and can be sepd. by crystn. of the quinine salt, or by boiling with concd. HCl , which gives the lactone of III and the acid II. II was resolved by means of the cinchonine salt, crystg. from EtOH . *d*-*Anti* acid, (*d*-II), $m. 214^\circ$, $[\alpha]_D^{20} 7.37$ (EtOH); *Na* salt, $[\alpha]_D^{20} 5.23$ (H_2O , c 19.02). *Quinine* salt, $m. 231^\circ$, $[\alpha]_D^{20} -127.2^\circ$ (EtOH , c 0.7451, d 1.891). *Quinidine* salt, $m. 141^\circ$, $[\alpha]_D^{20} 154.4^\circ$ (EtOH , c 5.417). *Acid cinchonine* salt, $m. 174^\circ$, $[\alpha]_D^{20} 115.2^\circ$ (EtOH , c 2.11). The *l*-acid, $m. 214^\circ$, has $[\alpha]_D^{20} -7.2$ (EtOH , c 0.76 to 1.32); 1.10 g. dissolve in 100 cc. EtOH and 0.5 g. in 100 cc. H_2O at 20° . *Na* salt, $[\alpha]_D^{20} -5.7^\circ$ (H_2O , c about 18). *Quinine* salt, $m. 225^\circ$, $[\alpha]_D^{20} -135.6^\circ$ (EtOH , c 1.057); *quinidine* salt, $m. 151^\circ$, $[\alpha]_D^{20} 162.4^\circ$ (EtOH , c 5.645); *cinchonine* salt, $3\text{C}_{19}\text{H}_{21}\text{ON}_2 \cdot 2\text{C}_{10}\text{H}_{17}\text{O}_6$, $m. 190^\circ$, $[\alpha]_D^{20} 145.7^\circ$ (EtOH , c 2.521). III was resolved by means of quinine. The *d*-*para* acid, $m. 206^\circ$, has $[\alpha]_D^{20} 9.12^\circ$ (EtOH , c 4.17) and 9.91° in H_2O (c 1.107). *Na* salt, $[\alpha]_D^{20} -4.63^\circ$ (H_2O , c 6.3). *Quinine* salt, $m. 207^\circ$, $[\alpha]_D^{20} -134.5^\circ$ (EtOH , c 2.98). This is the more sol. isomer. The *l*-acid, $m. 208^\circ$ and has $[\alpha]_D^{20} -9.6^\circ$ (EtOH , c 4.091) and -10.96° (H_2O , c 1.004). The *Na* salt showed $[\alpha]_D^{20} 4.41^\circ$ (H_2O , c 18.36). *Quinine* salt, $m. 213^\circ$, $[\alpha]_D^{20} -111.4^\circ$ (EtOH , c 2.074). No evidence has been found of the interconversion of the *anti* and *para*-forms.

C. J. WEST

Some preparations from maleic and fumaric acids. H. G. OGDY. *J. Am. Chem. Soc.* 45, 2156-60 (1923).— $\text{BzCH:CHCO}_2\text{H}$ was obtained in 95% yield from 3 g. maleic anhydride (I), 25 cc. C_6H_6 and 9 g. AlCl_3 kept cool for 20 min. and then heated 1.5 hrs. at 60° . From PhMe under the same conditions is obtained 77% *p*- $\text{MeC}_6\text{H}_4\text{COCH:CHCO}_2\text{H}$ (II), identified as the *p*-deriv. by boiling a few min. with 10% NaOH and oxidizing the resulting $\text{MeC}_6\text{H}_4\text{COMe}$ with cold alk. $\text{K}_2\text{Fe}(\text{CN})_6$ to *p*- $\text{MeC}_6\text{H}_4\text{CO}_2\text{H}$. *Me* β -*p*-toluylacrylate, from II with MeOH-HCl , $b_p 230-5^\circ$, $m. 45.4-16^\circ$. β -*p*-Toluy- α -chloropropionic acid, from II allowed to stand 60 hrs. in concd. HCl in a closed flask, $m. 144-4.5^\circ$. β -*p*-Toluy- α , β -dibromopropionic acid, from II and Br in cold AcOH . I and C_{10}H_8 in C_6H_6 with AlCl_3 heated, after 30 min., for 4 hrs. at $60-70^\circ$ give β - β -naphthylacrylic acid, $m. 189-90^\circ$, oxidized by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH on the H_2O bath to β - $\text{C}_{10}\text{H}_7\text{CO}_2\text{H}$; does not react with Br in cold AcOH and evolves HBr in hot AcOH ; *Me* ester, $m. 94-5^\circ$. β -*p*-Phenylbenzoylacrylic acid, obtained in 80% yield from I, Ph₂ and AlCl_3 in C_6H_6 at $60-70^\circ$, yellow, $m. 167-8^\circ$; *Me* ester, $m. 73.5-74^\circ$. β -*p*-Phenylbenzoyl- α , β -dibromopropionic acid, $m. 180-1^\circ$, gives *p*-Ph $\text{C}_6\text{H}_4\text{CO}_2\text{H}$ when fused 10 min. at 160° with KOH ; *Me* ester, $m. 120-1^\circ$. β -*meso*-Anthroylacrylic acid (10 g. from 8 g. I, 16 g. anthracene and 24 g. AlCl_3 in 100 cc. C_6H_6 at $60-70^\circ$), $m. 261^\circ$, does not react with Br in hot or cold AcOH , is not decompd. by fusion with KOH at 250° ; *Me* ester, $m. 149.5-50^\circ$. *trans*-Di-*p*-toluylethylene (IV), obtained in 52% yield from fumaryl chloride (III) and AlCl_3 in PhMe at room temp., light yellow, $m. 131.5^\circ$ (Conant and Lutz, C. A. 17, 283, give 148°), gives with Br in AcOH di-*p*-toluyl-*di*bromomethane (V), $m. 200-0.5^\circ$, which, fused with KOH at 130° , yields *p*- $\text{MeC}_6\text{H}_4\text{CO}_2\text{H}$. *cis*-IV, from the *trans*-form exposed to sunlight in AcOH for 3 days, $m. 152^\circ$, gives V with Br in AcOH . When the 134.5° -form is exposed to sunlight for 2 days in MgCO_3 the product after 1 recrystn. $m. 147^\circ$; further exposure to brighter sunlight for 2 days gives a small amt.

of a substance m. 120°, probably identical with C. and L.'s *cis*-compd. m. 123°. *trans*-2,4-Di-2,4-xyloylethylene, from *m*-xylene, yellow, m. 125.5-26° (yield, 15%), gives in AcOH with Br di-2,4-xyloxydibromoethane, m. 145°, which with KOH at 135° gives 2,4-Me₂C₆H₃CO₂H; *cis*-ethylene, from the *trans*-compd. (much of which is recovered unchanged) exposed to sunlight 1 week in MeOH, m. 65-5.5°. *trans*-Di-*p*-phenylbenzoyl-ethylene, from Ph₂, yellow, m. 247.5-48°, unchanged by 36 hrs.' exposure to sunlight in CHCl₃, gives with Br in CHCl₃ the dibromoethane, m. 218-8.5°. Rubidge and Qua's method for the prepn. of diphenylphthalide (C. A. 8, 1955) is not applicable to the prepn. of diphenylcrotonolactone from I, nor can the lactone be made from the anhydride of BrCH:CHCO₂H and AcOH.

C. A. R.

The synthesis of optically active asparagines. O. E. LUTZ. *J. Russ. Phys. Chem. Soc.* 48, 1881-7(1916).—Various optically active *N*-substituted asparagines are synthesized by the action of aromatic amines on *l*-thromosuccinamic acid. In this way, aniline gives *l*-phenylasparagine, m. 147-8°, anisidine gives *l*-anisylasparagine, m. 135°, and *m*-toluidine gives *l*-*m*-tolylasparagine, m. 160-1°. These substances slowly lose their *l*-rotatory power if kept for some time with mineral acids.

J. C. S.

Xanthyllallantoin. R. FOSSE AND A. HIEULLE. *Compt. rend.* 177, 199-202(1923).—By pptn. with xanthidrol, 0.001 g. allantoin may be detected in 1:1500 diln. in 66% HOAc (cf. C. A. 17, 3016). Its soly. in hot MeOH, and the formation of a cryst. *K* salt distinguish xanthyllallantoin from xanthylurea.

I. P. ROLF

The analysis of tuberculinic acid. E. B. BROWN AND T. B. JOHNSON. *J. Biol. Chem.* 57, 199-208(1923).—Tuberculinic acid was purified and analyzed for C, H, N, P and ash. It appears to be a trinucleotide containing adenine, thymine and cytosine, each of which was obtained from the purified product. Guanine is also a constituent of tuberculinic acid but was split from the original mol. in the process of purification. It was obtained from the filtrates.

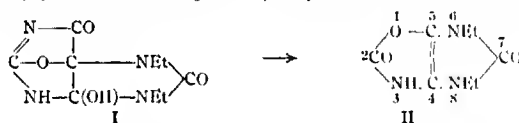
I. GREENWALD

Reduction of uric acid glycols. Characterization of their hydroxyls. HEINRICH BILTZ AND RUDOLF LEMBERG. *Ann.* 432, 137-76(1923).—Earlier attempts to reduce the glycols (C. A. 6, 2619) by means of HI gave hydantoins. Attempts to protect the 4-OH group by methylation showed that while the 5-OH could be methylated, the 4-OH was not reactive (C. A. 15, 1517). The possibility of replacing the HO group by Cl was next tried. 7,9-Dimethyluric acid glycol dissolves in POCl₃ but a chloride could not be isolated. Reduction with Zn and AcOH gives a 10-5% yield of dimethyluric acid; other reducing agents, such as HI, SnCl₄ and HCl, etc., were without action on the product. The reaction failed with the di-Et deriv. That only the 5-OH group reacts in this reaction is shown by the fact that the product with MeOH or EtOH yields the half ether. 7,9-Diethyluric acid-4,5-glycol Et half ether, m. 179°. Me ether, m. 130-1°. Uric acid glycol and POCl₃ yield spiro-5,5-dihydantoin. The 9-Me and -Et derivs. are decompd. Heated with PBr₃ at 95-105°, 7,9-diethyluric acid glycol (I) gives 7,9-diethyl-4-hydroxy-4,5-dihydrouic acid (II), m. 199-200°. The soly. in H₂O is about 6.5%. PCl₅ gives the same product but in smaller yields. It has a bitter taste but no pharmacol. action. *NH₄* salt, needles, which are completely hydrolyzed by concg. the aq. soln. One g. II, treated with Cl, gives 0.1 g. I, part of II suffering the caffeolinc decompn. In EtOH, Cl transforms II into the Et half ether; the Me half ether results if Cl is passed into a warm MeOH soln. of II. 4-MeO deriv., m. 200°, from II and CH₃N₂ by addn. of a drop of H₂O; soly. in H₂O, about 1.5%. Cl in MeOH gives the Me half ether. II, heated at 250° for 0.5 hr., gives HOCN and 1,3-diethylhydantoylamide, m. 110°, which is oxidized by Cl in aq. suspension to 1,3-diethyl-5-hydroxyhydantoylamide (the monohydrate of which m. 90-100°, and loses its H₂O at 105°) and to the 5-EtO deriv. by Cl in EtOH. I, allowed to stand with C₂H₅N and MeOH for 2 days, is changed to 1,3-dimethyl-5-hydroxyhydantoylurea. 7,9-Dimethyluric acid glycol and PBr₃ at 170° give 7,9-dimethyl-4-hydroxy-4,5-dihydrouic acid (III), m. 200-1°, soly. in MeOH, about 7 parts in 100. *NH₄* salt, easily decompd. by heating or by concg. an aq. soln. Cl in EtOH or MeOH gives the corresponding half ethers. Conc'd. with HCl, 1,3-dimethylhydantoin results. 4-Methoxy deriv., with 1 H₂O, m. 190-5°; Cl in MeOH transforms it into the Me half ether. Thermal decompn. of III gives HOCN and 1,3-dimethylhydantoylamide, m. 181°, which is oxidized to the 5-HO deriv., m. 185°. The monohydrate, m. 180-2°. The 9-Et, 9-Me and 3,7-Me₂ glycols could not be reduced by the above method. 3,7-Dimethyl-4-methoxy-4,5-dihydrouic acid, m. 193-4°. The action of heat on the corresponding 4-HO deriv. gives a compd., C₈H₁₀O₂N₂, which is not the expected 1-methylhydantoylamide but contains an extra Me group. 3,7-Dimethyluric acid glycol with C₂H₅N and MeOH gives 1-methyl-5-hydroxyhydantoyl-9-methylurea, n. 200-1°, though in very poor yield.

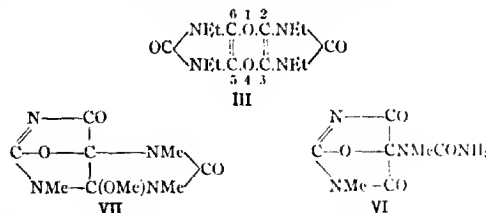
C. J. WEST

Dioxine decomposition of the 4-hydroxy-4,5-dihydrouic acids. HEINRICH BILTZ

AND RUDOLF LEMBERG. *Ann.* **432**, 177–207 (1923); cf. preceding abstr. 7,9-Diethyl-4-hydroxy-4,5-dihydrouric acid in $C_4H_8N_2$ is oxidized by a stream of air during 1–2 hrs. (until needle-like crystals have changed to rhomboids or 6-sided forms) to 7,9-diethyl-4-hydroxy-6,8-dioxo-2,5-oxidopurine-3,1,5,6,8,9-hexahydrate (I, m. 200–10° (decompn.)). The same change occurs if the $C_4H_8N_2$ soln. stands in the air for 1–2 days, or by oxidation of the acid by $Ag_2O \cdot NH_4OH$ or 10% $FeCl_3 \cdot K_2Cr_2O_7$ gives not I but the uric acid glycol. Oxidation by the air takes place in MeOH after several weeks; it is accelerated by the addn. of $C_4H_8N_2$. I is readily methylated by CH_3N_2 , giving the *p*-MeO deriv., m. 198°, also obtained by oxidizing 7,9-dimethyl-4-methoxy-1,5-dihydrouric acid with $FeCl_3$. When 5 g. I are heated with 200 cc. H_2O until soln. results (0.75 hr.), CO_2 and later NH_3 are evolved and there results the lactone of 1,3-diethyl-5-hydroxyglyoxalono-4-carbamic acid (1,3-diethyl-4',5',4,5-oxazolono-2'-glyoxalono-2)], (II), m. 116–8° (decompn.). A by-product of this reaction is 2,3,5,6-bis-[N,N'-diethylglyoxalono]-1,4-dioxine (III), m. 165–6°. It does not react with I_2 or $PhNH_2$, is pptd. unchanged from boiling HNO_3 by H_2O , but is decompd. by boiling concd. KOH, splitting off $EtNH_2$. II is transformed into III by heating 2 min. with 2 *N* Na_2CO_3 or NH_4NO_3 , or 5% NaOH, and III also results from I and 10% Na_2CO_3 . Oxidation of III gives diethylparabanic acid. CH_3N_2 reacts with III to give the 4-methylcarbamic acid deriv., $C_{11}H_{15}O_4N_5$, m.



228–9°. $MeNH_2$ is evolved on heating with NaOH. The 7,9-dimethyl deriv. (IV) corresponding to I, m. 230°, is most conveniently prepd. by oxidation with 10% $FeCl_3$. Oxidation proceeds more readily than in the Et series, being observed in crystg. the uric acid from MeOH. The *p*-MeO deriv., m. 230° (decompn.), results by the action of CH_3N_2 or the oxidation of the corresponding uric acid. The lactone corresponding to II could not be isolated; heating with water decomp. IV to 2,3,5,6-bis-[N,N'-dimethylglyoxalono]-1,4-dioxine, m. 228°, which is oxidized to dimethylparabanic acid. The 3,7-dimethyl deriv. (V) corresponding to I, decomp. 186°, results only when the uric acid is oxidized with 5% $FeCl_3$. Boiling V with H_2O easily isomerizes it to 3-methyl-4,6-dioxo-2,5-oxido-5-[α -methylurido]pyrimidine-3,4,5,6-tetrahydra (VI), decomp. 245°; soln. in 10% NaOH and boiling for 5 min. gives V, which seps. on acidification. Either V or VI, with CH_3N_2 , gives 3,7,9-trimethyl-1-methoxy-6,8-dioxo-2,5-oxidopurine 3,4,5,6,8,9-hexahydrate (VII), decomp. 178–9°. The 3,7-dimethyl-4-methoxy deriv. VII with CH_3N_2 , 1-Methyl-5-hydroxyglyoxalono-4-methylcarbamic acid lactone (VIII),



decomp. 263–4°, results by longer boiling of V with H_2O ; oxidation gives methylparabanic acid. CH_3N_2 introduces a Me group in the 3-position, giving the 1,3-dimethyl deriv., m. 172–3°. VIII does not readily yield a dioxine, it being necessary to boil it with 20% KOH or concd. HCl for 0.5 hr. 2,3,5,6-Bis-[N-methylglyoxalono]-1,4-dioxine, darkens 300°, decomp. 327°, and is oxidized to methylparabanic acid. CH_3N_2 adds 1 Me group, giving the *N,N'*-di-Me deriv., m. 228°.

C. J. WEST
o-Diaminopyrimidines and their transformation into purines. WILHELM TRAUBE, FRIEDRICH SCHÖTLÄNDER, CARL GOSLICH, ROBERT PETER, F. A. MEYER, HEINRICH SCHLÖTER, WILHELM STEINBACH AND KARL BREDOW. *Ann.* **432**, 266–96 (1923).—4,6-Diamino-2,6-dihydropyrimidine sulfate (I) and $KCNO$, heated in H_2O 1.5 hrs.,

yield 4-amino-5-carbamino-2,6-dihydroxypyrimidine, fine needles, sol. in NH_4OH and alkalies; boiling in acids gradually splits off NH_3 , which also occurs upon heating to 230° , with the formation of uric acid. **I** and PhCNO give the *phenylurea*, difficultly sol. needles, which is transformed into 9-phenyluric acid by heating 0.5 hr. with 20% HCl . In the same way, the addn. product of PhNCS yields 9-phenyl-8-thio-2,6-dihydroxypurine. 3-Methyl-4-amino-5-acetyl-amino-2,6-dihydroxypyrimidine, fine needles with 2 H_2O of crystn., which are lost at 130° . Transformed into the Na salt and the latter heated at $230-40^\circ$, there results 3,8-dimethylxanthine, fine needles with 1 H_2O , lost at 140° . 3-Methyl-4,5-diamino-2,6-dihydroxypyrimidine and PhNCS yield a *phenylthiourea deriv.*, with 1.5 H_2O of crystn.; heated 1 hr. with 20% HCl this is transformed into 3-methyl-8-thio-9-phenyluric acid, small leaflets, from which the S cannot be removed by warming the alk. soln. with Ph(OAc)_2 . This is carried out by heating with dil. HCl and NaNO_2 , giving 3-methyl-9-phenylxanthine, needles. 3-Methyl-2,6-dihydroxy-4-amino-5-oxalamino-2,6-dihydroxypyrimidine, long needles in nearly theoretical yield by adding 1 part of the pyrimidine to 5 parts molten $(\text{CO}_2\text{H})_2$, crystals with 1 H_2O , reduces Ag sol. on warming, and gives upon evapn. with fuming HNO_3 a purple-red residue. The di-Na salt, heated at $250-60^\circ$ for 6-8 hrs., gives 3-methylxanthine-8-carboxylic acid, needles, with 1.5 H_2O . The Ag salt is amorphous but the Pb and Ba salts are cryst. The pure yellow residue upon evapn. with HNO_3 turns violet when moistened with KOH . At 160° it loses CO_2 and gives 3-methylxanthine. 3-Methyl-2,6-dihydroxy-4-amino-5-cyanoacetaminopyrimidine, glistening needles. Four mols. of NaOH (2 N) transforms this into 3-methylxanthine-8-acetic acid, needles with 1 H_2O . Me ester, needles. The corresponding 5-succinaminopyrimidine forms needles with 1 H_2O , and is transformed by heating the Na salt at $250-60^\circ$ into 3-methylxanthine-8-propionic acid, crystals with 1 H_2O lost at 130° . Et ester, needles. 1,3-Dimethyl-4,5-diamino-2,6-dihydroxypyrimidine, heated with an excess of Ac_2O for several hrs., yields 1,3,8-trimethylxanthine, rhombic prisms, sol. in 25-30 parts boiling H_2O , has a bitter taste and gives a pure yellow residue with concd. HNO_3 . 1,3-Dimethyl-2,6-dihydroxy-4-amino-5-cyanoacetaminopyrimidine, needles, which reduce $\text{NH}_4\text{OH-Ag}_2\text{O}$ and give a red residue with HNO_3 . Heated with 4 mols. 8% NaOH it gives *theophyllineacetic acid*. 2,4,5-Triamino-6-hydroxypyrimidine monoacetate, by heating the base with 5-10 parts AcOH 3 hrs., crystals with 1 H_2O . The Na salt, heated 2 hrs. at $220-40^\circ$, gives 8-methylguanine, prisms; HCl salt, prisms with 1 H_2O . Sulfate, tables. ~~Ureale~~, oval leaflets. 8-Ethylguanine, micron needles; HCl salt, prisms. 2,4-Diamino-6-hydroxy-5-succinaminopyrimidine, yellowish needles; heating the Na salt 5 hrs. at $250-60^\circ$ gives *guanine-8-propionic acid*, needles, which gives a pure yellow residue with concd. HNO_3 . Et ester HCl salt, needles with 1 H_2O , characterized by a sweet taste. 2-Methyl-4-amino-6-hydroxypyrimidine, m. 290° , results from acetamide and $\text{CNCH}_2\text{CO}_2\text{Et}$ and crystals with 1 H_2O . HCl salt, transparent rods. This is transformed into the *isonitroso compd.*, $\text{C}_7\text{H}_6\text{N}_4\text{O}_2$ (74% yield), dark green crystals; the Na salt is pale violet, the K salt violet. Reduction of this gives 2-methyl-4,5-diamino-6-hydroxypyrimidine, glistening leaflets with 1 H_2O (85% yield), which reduce $\text{NH}_4\text{OH-Ag}_2\text{O}$ in the cold; HCl salt, rhombic tables; sulfate. Heated with 99% HCO_2H for several hrs., 2-methylhypoxanthine results. One part dissolves in about 100 parts cold and 35 parts boiling H_2O . HCl salt, transparent prisms; sulfate, columns. Na salt, monoclinic crystals. Warmed in EtONa with MeI , there results a double compd. of NaI and 1,2,7-trimethylhypoxanthine, $\text{C}_7\text{H}_5\text{N}_4\text{O.NaI.3H}_2\text{O}$, which becomes yellow in the air and from which the free base is liberated by treatment with Ag_2O and subsequent removal of the NaOH with CO_2 . **I** and BzH give 4-amino-5-benzylamino-2,6-dihydroxypyrimidine, felt-like needles, which is reduced by 2% Na-Hg to the corresponding benzyl compd., m. 265° , leaflets, which reduces Fehling and Ag solns. Sulfate, prisms or leaflets. Heated with HCO_2H this yields 7-benzylxanthine, m. 295° (decompn.), an intermediate product being the *formyl deriv.*, which is heated at 280° until loss in wt. ceases. 1-Methyl-7-benzylxanthine, m. 250° , by the action of 1 mol. MeI ; if 2 mols. Me_2SO_4 are used, the 1,3- Me_2 deriv., m. 158° , results. 3-Methyl-5-benzylamino-4-amino-2,6-dihydroxypyrimidine, m. 226° . Heated with HCO_2H this yields a *formyl deriv.*, m. 252° , which, held at its m. p., loses 1 H_2O and gives 3-methyl-7-benzylxanthine, m. 273° . C. J. WEST

Mercaptans of the purine group. P. C. RAY, G. C. CHAKRAVARTI and P. K. BOSE. *J. Chem. Soc.* 123, 1957-62 (1923).—KHS in boiling EtOH does not react with 2,6-dichloro-8-hydroxypurine in the expected way, the K salt of the purine sepp. In H_2O at 100° a mixt. is obtained but pure products could not be isolated. At $140-50^\circ$ for 3 hrs., however, 2,6-dithiol-8-hydroxypurine, yellow nodules, is formed as the Na salt, fine needles. Di-Me ether, m. $285-8^\circ$ (decompn.), by heating the Na salt with excess of MeI . 2-Chloro-6-thiol-8-hydroxy-7,9-dimethylpurine, brownish yellow rhomboids,

results by heating the 2,6-Cl₂ deriv. with EtOH-H₂S for 15 min. It is a strongly monobasic acid, bitter to the taste, odorless, decomps. without melting. *K* salt, needles. *NH₄* salt, silky crystals. Heated with HgCl₂ in AmOH, the mercaptan yields a *chloromercaptide*, C₇H₄ON₂Cl₂SHg.4EtOH, insol. in AmOH, which permits the sepn. of the 2nd product of reaction, the *compd.* C₇H₄ON₂Cl₂SHg, needles. With 1 in K₂I, the mercaptan yields a *disulfide*, C₇H₄O₂N₂Cl₂S₂, m. 259°. The *K* salt and MeI give the *Me ether*, m. 179°. *Et ether*, m. 133°. *Pr ether*, m. 120°. Heated with PhNHNH₂, the mercaptan gives a *phenylhydrazino deriv.*, C₇H₄ON₂S, needles. 2,6-Dithiol-8-hydroxy-7,9-dimethylpurine, yellow, m. above 300° (decompn.), results by heating the 2,6-Cl₂ or the Cl-mercaptan deriv. in a sealed tube at 130-40° for 3 hrs. *K* salt, silky needles. *Di-Me ether*, m. 172-3°. *Di-Et ether*, m. 101°. *Dibenzyl ether*, m. 158°. The fact that these compds. yield only a mono-*K* salt indicates that one of the thiol groups is in the keto form.

C. J. WEST

The influence of some normal salts on the mutarotation and specific rotation of glucose. HANS MURSCHHAUSER. *Biochem. Z.* 136, 66-70 (1923); cf. *C. I.* 16, 2118. In retarding mutarotation the alkali halides (except NH₄Cl) are more effective than the alkali nitrates (except NH₄NO₃). NH₄Cl, (NH₄)₂SO₄, MgSO₄ and the alkali acetates accelerate mutarotation. 2 *N* solns. of BaCl₂ and CaCl₂ accelerate, 1 *N* or 1 *N* solns. retard, mutarotation. The sp. rotation is decreased by the alkali halides (including NH₄). It is increased by the alk. earth halides (except Mg). MgCl₂ and the alkali acetates do not affect the sp. rotation of glucose in distd. H₂O.

G. R. S.

The preparation and constitution of synthetic fats containing a carbohydrate chain. HELEN S. GILCHRIST. *Rept. Brit. Assoc. Advancement Sci.* 1922, 357. A study of the products of carbohydrate chains and unsatd. groups present in natural fats. When α-Me glucoside and mannitol react (in the presence of NaOEt) with the oleyl residues of olive oil, a monooleate is formed initially in the 1st case, whereas in the 2nd case 2 oleyl groups enter the hexitol chain. The condensation is immediately followed by internal dehydration (loss of 1 mol. H₂O), the fatty residues remaining intact. *Anhydromethylglucoside monooleate* and *mannitan dioleate* are definite compds. On methylation they yield *mono-Me derivs.* which are unstable in the high vacuum of the Gaede pump. On heating with acid alc., the methylated compds. give *Me oleate* and an *alkylated sugar deriv.*, the anhydro ring persisting during hydrolysis. C. C. DAVIS

Unsaturated reduction products of sugars and their transformations. VI. 3-Hydroxyacetobutyl alcohol, a simple ketose. MAX BERGMANN AND ARTHUR MURKLEY. *Ann.* 432, 319-44 (1923); cf. *C. A.* 17, 3166. The oxidation of 15 g. anhydroacetobutyl alc. (I) with 21.11 g. BzO₂H in dry Et₂O gives a 47% yield of the *anhydride* (II), b_p 56.5-7.5°, d₄²⁰ 1.0331, n_D²⁰ 1.4441, of 3-hydroxyacetobutyl alc. (III). It reduces Fehling soln. but not as readily as III. *Phenylhydrazone*, m. 85-6°. III, obtained by the oxidation of I with BzO₂H in moist Et₂O, b_p 113-4°, m. 73°. One g. reduces 160 cc. Fehling soln. The *osazone* is pure yellow and m. 133°. II is obtained by distg. III with BzOH at 15 mm. The reverse transformation is brought about by heating with *N* H₂SO₄ 2 hrs. 0.01 *N* MeOH-HCl reacts with III to give the *methyl cyclonetal* (2-methoxy-2,6-oxido-3-hydroxyhexane), b_p 76-7°, d₄²⁰ 1.0813, n_D²⁰ 1.4512. It decolorizes alk. or neutral KMnO₄, scarcely reduces Fehling soln., and is quant. decompd. by 0.01 *N* HCl in 1 hr. The reaction with 0.01 *N* MeOH-HCl is 92.1% complete after 10 min., with 0.002% *N* HCl, 29% after 30 min., and with 0.001 *N* HCl, 23.6% after 30 min. The rate of hydrolysis was detd. as follows: 0.01 *N* HCl at 0°, 23% after 30 min., 100% after 60 min.; at 18°, with 0.001 *N* HCl, at 25°, 68% after 60 min., and at 100°, 78% after 10 min. Heating 12 g. II with 120 cc. 0.1 *N* MeOH-HCl for 3 hrs. gives the *methyl cyclonetal* of 3-methoxyacetobutyl alc. (2,3-dimethoxy-2,6-oxidoheptane) (IV), b_p 69-70°, d₄²⁰ 1.0300, n_D²⁰ 1.4405. If the prepn. is carried out in the cold with *N* MeOH-HCl, the value of n_D²⁰ is 1.4442. Warmed with 0.1 *N* HCl 1 hr. at 50°, 3-methoxyacetobutyl alc., b_p 88-90°, is formed, which reduces Fehling soln. only slightly at boiling temp. Oxidized with CrO₃, IV yields 3-methoxyacetobutyric acid, b_p 115°. H₄C(CN)₄ reacts with acetobutyl alc. in H₂O to form an *oxonium salt*, which acts as a catalyst in the methylation with MeOH. I reacts similarly. 3-Bromoacetobutyl alc. (V), b_p 70-5°, results from 20.6 g. Br and 15 g. acetobutyl alc. at 0°. It has a burning action on the skin, reduces Fehling soln. when heated, and is completely decompd. after several days' exposure to the air. Heating with H₂O splits off HBr, yielding an *anhydride* (VI) of III, b_p 50-1°, b_p 63-4°, n_D²⁰ 1.4381, which differs from II in that a *cryst. phenylhydrazone* could not be obtained. V reacts with PhNHNH₂, HBr being split off, if the mixt. is warmed, the resulting *osazone* is identical with that from III. V, with MeOH-HCl, yields a *cyclomethylacetal* (2-methoxy-3-bromo-2,6-oxidoheptane), b_p 78-81°. VI

$[\alpha]_D^{20} -34.10^\circ$ (acetate, m. 124°); the other m. 134.5° , $[\alpha]_D^{20} -33.61^\circ$ (acetate, m. 119°). Linseed oil likewise contains at least 2 phytosterols: one m. 138° , $[\alpha]_D^{20} -31.22^\circ$ (acetate, m. $129-30^\circ$); the other m. around 131° , $[\alpha]_D^{20} -31.16^\circ$ (acetate, m. 121°). None of the above phytosterols contained 1 mol. H_2O of crystal; the loss in wt. on drying was somewhat irregular but corresponded more nearly to 0.5 mol. H_2O . C. A. R.

Recent investigations on substitution in the benzene nucleus. A. F. HOLLEMAN. *Rec. trav. chim.* **42**, 355-79 (1923).—A lecture delivered at Univ. of London and Oxford which is the only existing review in English of the recent work of H. and his pupils on the replacement of substituents already present in the C_6H_5 ring. E. J. WITZEMANN.

Some reactions of tetranitroaniline. C. W. DAVIES AND T. C. JAMES. *Aberystwyth Studies* **4**, 213-6 (1922).—Tetranitroaniline does not form compds. with hydrocarbons in dry benzene or acetone soln. With phenols, there is a slight color change but only with β -naphthol was a definite compd. obtained, $Ca(NO_2)_4NH_2 \cdot C_{10}H_7O$, deep red, beginning to decomp. at 110° , m. 140° . With primary amines, tetranitroaniline rapidly condenses with elimination of the $3-NO_2$ group. With aniline, 2,4,6-trinitro-3-aminodiphenylamine is formed, orange-yellow, m. 188° . *o*-Toluidine gives 2,4,6-trinitro-3-aminophenyl-*o*-tolylamine, dark red, m. 200° ; 2,4,6-trinitro-3-aminophenyl-*m*-tolylamine, brick-red, m. 181° , and 2,4,6-trinitro-3-aminophenyl-*p*-tolylamine, orange, m. 220° . 2,4,6-Trinitro-3-aminophenyl- β -naphthylamine, bright red, m. 212° ; from acetone it forms bright yellow crystals contg. 1 mol. of acetone which is lost at 70° . When tetranitroaniline is warmed with *n*-AmOH, 2,4,6-trinitro-3-aminophenyl amyl ether is obtained, yellow, m. 168° . Trinitro-*m*-phenylenediamine is formed when tetranitroaniline is warmed with NH_4OH . J. C. S.

Derivatives of straw lignin. H. F. PASCHKE. *Cellulosechemie* **4**, 31-2 (1923); cf. C. A. **16**, 1567.—Straw lignin (prepn. and methods of purification not given) condenses with 3 mols. $PhNH_2$ in the presence of $(CO_2H)_2$ after heating under reflux, to form the deriv. $C_{32}H_{32}N_6O_{16}$, purified(?) by reprecip. from C_2H_5Cl . Lignin melted with Na_2S and S formed a dye, $C_{24}H_{16}S_6O_4$. No methods of purification are given. The dye is not a substantive for cotton. Lignin is believed to have aldehyde groups in the mol. since in alk. soln. it converts hide into soft leather. (Exptl. data are very meager, and results are probably not reproducible.—ABSTR.) LOUIS E. WISE

Bromination of 2-amino-*p*-xylene and certain new azo dyes. A. S. WHEELER AND E. W. CONSTABLE. *J. Am. Chem. Soc.* **45**, 1999-2001 (1923).—The Br in Fischer and Windaus' bromo-2-amino-*p*-xylene (I) (*Ber.* **33**, 1974 (1900)) has been definitely located in position 5. 2-Acetamino-5-bromo-*p*-xylene, from 1,4,2- $C_6H_3Me_2NH_2$ Ac and Br in AcOH, m. 187° ; 1 g. dissolves in 8 cc. of hot alc.; with hot HBr (d. 1.3) it yields 2-amino-5-bromo-*p*-xylene- HBr , m. 255° (decompn.), the free base of which is identical with I and which on diazotization and treatment with Cu powder and KBr gives 1,4,2,5- $C_6H_3Me_2Br_2$, m. 75.5° ; this with HNO_3 above 300° gives 2,5,1,4- $C_6H_3Br_2(CO_2H)_2$, m. 313° , whose di-Et ester m. 125° . 2,4-Bis-[5-bromo-2-*p*-xylyloxy]phenol, from I, HBr , diazotized and treated with 0.5 mol. $PhOH$ in the minimum amt. of dil. alkali, dark brown scales with metallic luster when viewed in the mass, pale green under the microscope, m. $233-4^\circ$, dyes silk ceru and wool orange brown by the development method of application; resorcinol compd., claret-brown, m. 263° , dyes silk ceru and wool Brazil red; α -naphthol compd., very dark brown to black, m. $222-3^\circ$, dyes silk Mars orange and wool claret-brown. 1-[5-Bromo-2-*p*-xylyloxy]- β -naphthol, from diazotized I, HBr and 1 mol. β -naphthol, scarlet-red, dyes silk light red and wool Nopal red. C. A. R.

The action of reducing agents on some polynitrodiphenylamines. N. M. CULLITANE AND T. C. JAMES. *Aberystwyth Studies* **4**, 209-12 (1922).—Reduction of 2,4,6- $(O_2N)_3C_6H_2NHPh$ with alc. $(NH_4)_2S$ gives the known 1,3-dinitro-5,10-dihydrophenazine. It forms a *di-Ac deriv.*, $C_{16}H_{12}O_4N_4$, yellow, m. above 320° , and a *di-Bz deriv.*, $C_{20}H_{16}O_4N_4$, yellow, m. 230° (decompn.). As an intermediate compd. in the reduction, 2,4-dinitro-6-aminodiphenylamine was obtained, yellow, m. 176° . Reduction of picrylaniline with $SnCl_4$ gives a black powder dissolving in concd. H_2SO_4 with a violet color. By reduction of picryl-*p*-toluidine with alc. $(NH_4)_2S$, 6,8-dinitro-2-methyl-5,10-dihydrophenazine was obtained, bright yellow, m. above 340° . The constitution of this substance was confirmed by prep. it from picryltolylendiamine (C. A. **15**, 234) by heating until nitrous fumes were no longer evolved. Reduction of picryl-*m*-toluidine with alc. $(NH_4)_2S$ appears also to give a dihydrophenazine deriv. J. C. S.

Action of hydroxylamine and of dihydroxyammonia on certain nitroso derivatives. A. ANGELI AND ANTONIO PIERONI. *Atti accad. Lincei* [v] **32**, i, 151-3 (1923).—From the analogies in behavior shown by 2 groups when directly united and when occupying *o*- or *p*-positions in an aromatic nucleus (C. A. **12**, 365; **15**, 523), it is to be expected that

aromatic compds. of the form $\text{NHRC}_6\text{H}_4\text{NH}_2$, $\text{NHRC}_6\text{H}_4\text{NO}$, or $\text{NR}:\text{C}_6\text{H}_4:\text{NOH}$ would, in some reactions, behave similarly to the hydrazines or diazo-hydrates. When treated with HNO_3 , amines of the 1st of the above forms give, not the corresponding diazonium salts, but compds. of the probable formula $\text{NR}:\text{C}_6\text{H}_4:\text{N}_2$ (cf. Ikuta, *Ann.* 243, 272-89), which may be regarded also as derivs. of diazoiminoquinone, $\text{NR}:\text{C}_6\text{H}_4:\text{N}:\text{N}$. Further, since diazonium hydroxides are converted by the action of NH_2OH into the corresponding azides, $\text{RN}_2\text{OH} + \text{NH}_2\text{OH} = \text{RN}:\text{N}:\text{N} + 2\text{H}_2\text{O}$, the action of this reagent on NO-derivs. of the type $\text{NHRC}_6\text{H}_4\text{NO}$ should furnish either diazoiminoquinone or a very simple deriv. of it. This is actually found to be the case. The action of NH_2OH on $p\text{-ONC}_6\text{H}_4\text{NHPh}$ in alk. soln. yields a *compd.*, $\text{C}_{12}\text{H}_{10}\text{N}_4$, pale brown, m. 71° , and on reduction with tin and HCl gives the amine, $\text{NHPhC}_6\text{H}_4\text{NH}_2$. The formula $\text{NH}:\text{NPh}:\text{C}_6\text{H}_4:\text{N}:\text{N}$ being unlikely, this *compd.* has probably the structure $\text{NHPhC}_6\text{H}_4\text{N}:\text{N}:\text{N}$ or $\text{NPh}:\text{C}_6\text{H}_4:\text{N}:\text{N}:\text{NH}$, the diazo *compd.*, $\text{NPh}:\text{C}_6\text{H}_4:\text{N}:\text{N}$, first formed undergoing reaction with 2nd mol. of the NH_2OH . Similarly, the action of NH_2OH on the NO *compd.*, $\text{NHMeC}_6\text{H}_4\text{NO}$, yields a *cryst. compd.*, m. 52° . Both these *compds.*, for which the name *photo-azides* is suggested, exhibit sensitiveness towards light resembling that of Ag salts. Paper moistened with a dil. benzene soln. of the Ph deriv. and exposed to light rapidly turns violet and then black; with the Me deriv., first a red and afterwards a violet coloration is obtained. Dihydroxyammonia, obtained from benzosulfohydroxamic acid and an alkali, acts readily on $p\text{-ONC}_6\text{H}_4\text{NHPh}$ in alk. soln., yielding an acid *compd.*, deep yellow, m. 74° , undergoes rapid alteration when either heated or exposed to light. J. C. S.

The formation of accessory products in diazotization according to the method of Witt. L. ERLON. *Rec. trav. chim.* 42, 145-83 (1923).—Witt's method (C. A. 3, 2942) of diazotization: $\text{K}_2\text{S}_2\text{O}_8 + 2\text{HNO}_3 \longrightarrow \text{K}_2\text{S}_2\text{O}_7 + 2\text{HNO}_2$ was devised for use with feebly basic amines. In attempting to obtain 3,5-Br $_2$ C $_6$ H $_3$ CO $_2$ H (I) by diazotization and reduction from 3,5,4-Br $_2$ (NH $_2$)C $_6$ H $_3$ CO $_2$ H (II), E. obtained 3,5-Br $_2$ C $_6$ H $_3$ NO $_2$ (III) as well as I. II with HNO_2 gives 3,5,4-Br $_2$ (NHNO $_2$)C $_6$ H $_3$ NO $_2$ (IV). IV is first formed by the action of HNO_2 and then undergoes diazotization, giving rise to the III. These expts. were extended to 5 other *compds.*: 3,5,4-Br $_2$ (NH $_2$)C $_6$ H $_3$ CHO (V), 3,5,4-Br $_2$ (NH $_2$)C $_6$ H $_3$ COMe (VI), 3,5,6-Br $_2$ (NH $_2$)C $_6$ H $_3$ CO $_2$ H (VII), 3,5,4-(NO $_2$) $_2$ (NH $_2$)C $_6$ H $_3$ CO $_2$ H (VIII), 3,5,4-Cl $_3$ (NH $_2$)C $_6$ H $_3$ CO $_2$ H (IX). In all cases the Witt reaction gave rise to remarkable results. Of the above II, V, VI and IX behave similarly in this diazotization. In the accessory products, III for II, V and VI and 3,5-Cl $_2$ C $_6$ H $_3$ NO $_2$ (X) for IX, resp., the radical *p*- to the NH $_2$ is replaced by the NO $_2$ group. This replacement was established for the CHO and COMe groups in the presence of 2 Br atoms in the *o*-position and for the CO $_2$ H group in the presence of either 2 *o*-Br or 2 *o*-Cl atoms. In the case of VII the accessory reaction is less simple. It is the *o*-CO $_2$ H in VII that is replaced by the NO $_2$ group. In addition there is an intramol. transposition between the *o*-NO $_2$ group and the *p*-Br atom, so that 3,5,4-Br $_2$ (NHNO $_2$)C $_6$ H $_3$ NO $_2$ is the intermediate product. The diazonium *compd.* of VIII decomps. spontaneously, evolving N, before EtOH has occasion to reduce it, so that the NH $_2$ group is replaced in this case by OH and not by H. This constitutes a striking difference between VIII and II, V, VI and IX. This instability differs from that usually encountered with diazonium *compds.* The *o*-group is more often replaced by the action of H $_2$ O while the diazoic group remains intact. *A propos* these results Fuchs (C. A. 9, 1463) eliminated the NH $_2$ from PhNH $_2$ derivs. by the method of Witt. He treated VI in this way without observing any accessory products. It is possible that F. overlooked the accessory products especially in the case of 3,5,2-Br $_2$ (NH $_2$)C $_6$ H $_3$ CHO and 3,5,2-Br $_2$ (NH $_2$)C $_6$ H $_3$ COMe, since II gave accessory products. In interpreting the formation of these accessory products, E. studied the action of concd. HNO_2 on the 6 *compds.* above. In each case there was formed a nitrated nitramine in which the NO $_2$ group displaces the group in the I-position and these then undergo diazotization. V gives 2 nitramines of which 1 still contains the CHO group. It is probable that this nitramine by further nitration gives a nitrated nitramine so that it is the side chain and not the C $_6$ H $_3$ ring that is first attacked. According to Zincke's interpretation (*Ann.* 339, 204 (1904)) the reaction ought to take place in the opposite sense. The displacement of the CO $_2$ H in II is accompanied by a liberation of CO $_2$; in the case of the CHO in V CO and a little CO $_2$ is evolved. In the case of VI AcOH is formed. This is a displacement not previously reported in the literature. The action of HNO_2 on VII gives rise to CO $_2$. The velocity of displacement is different in various cases. In the nitration of II, V, VI, IX and VII a small amt. of the diazonium *compd.* is formed probably by a transformation of a part of the HNO_2 into HNO $_3$. There is considerable similarity between these 6 nitrations and the nitration of aminosulfobenzoic acid (Zincke, *et al.*, *Ann.* 339, 202 (1905)). They

found that 1,3-aminosulfobenzoic acids are transformed into nitrodiazonium compds. without loss of the sulfo group, while the 1,2- and 1,4-derivs. lose this group giving nitronitramines and diazonium salts. The nitrations studied by E. show that it is possible to extend this rule. The substituents, however, influence the results as shown in the nitration of VII. It gives a nitramine that still contains its CO₂H which conforms to the absence of an accessory product in the diazotization. The results of the action of HNO₃ led E. to suspect that the accessory reaction in the diazotization takes place in such a way that the compd. used is first converted into a nitramine, which in turn is diazotized and reduced, giving rise to an accessory product. Accordingly E. attempted to transform IV into III by Witt's method and succeeded. The diazotization of a nitramine being fundamentally a reduction it seemed possible to effect the transformation of IV into III by the use of EtOH: this was done and at the same time E. showed the diazotization is accompanied by a denitration. The displacement of the CO₂H, CHO and COMe groups in the *o*- and *p*-positions with respect to the NH₂ group observed in the action of HNO₃ is in harmony with the interpretation of Blankens (Rec. trav. chim. 23, 204(1904)). This displacement takes place easily in the presence of NH₃, NHR, OH, OR and Me groups (de Lange, Thesis, Leyden p. 101(1922)). The following are new compds.: 3,5-dichloro *p*-aminobenzoic acid, m. 291°, was obtained by the chlorination of *p*-NH₂C₆H₄CO₂H in glacial AcOH + concd. HCl. The yield is smaller than with II because much *sym*-Cl₂C₆H₄NH₂ is formed. 3,5-Dinitro-*p*-nitroaminobenzoic acid, softens 80°, decomps. 135-6°. The prepn. of 3,5-dinitroaminobenzene, yellow, m. 77°, is described in full.

The Witt method of diazotization. WALTER FUCHS, Rec. trav. chim. 42, 511-2 (1923).—F. replies to the comments made in the above abstract on the results previously obtained by him. He states that E. used far too much HNO₃ and that the accessory products obtained by him are due to a modification of the Witt method. E. has also failed to work up his diazo soln. according to the procedure recommended by Witt. F. gives the correct procedure here.

Diazotization according to the method of Witt. L. ELION, Rec. trav. chim. 42, 513-5(1923).—A reply to the above comments of Fuchs in which E. shows that the accessory products are due not to the amt. but to the concn. of the HNO₃ used. E. quotes data and statements from F.'s previous writings in support of his interpretation of the Witt method and of his contention that F. overlooked the formation of an accessory product in these diazotizations.

The influence of some substituents in the benzene ring on the mobility of chlorine of the side chain in relation to the problem of substitution in the benzene ring. III. S. C. J. OLIVIER, Rec. trav. chim. 42, 516-23(1923).—Having studied the influence of the substituents Me, Cl, Br and NO₂ present in the C₆H₄ ring on the mobility of Cl in the side chain O, has now begun to study the effects of CO₂H and I under the same conditions. *p*-ClCH₂C₆H₄CO₂H (I) was obtained thus: *p*-MeC₆H₄NH₂ by Sandmeyer's reaction gave *p*-MeC₆H₄CN, which was chlorinated (Mellinshoff, Ber. 22, 3208(1889)), giving *p*-ClCH₂C₆H₄CN; the latter on hydrolysis (M., Ber. 22, 3211, 3213(1889)) by way of the amide gave I m. 202.5-203°. The velocity of sapon. of I and the other CO₂H and I derivs. here described was detd. by the method previously used (Olivier, Rec. trav. chim. 41, 303(1922); cf. C. A. 16, 2851). *m*-ClCH₂C₆H₄CO₂H (II), prep. like I, m. 137.5-8.5°. Attempts to obtain *o*-chloromethylbenzoic acid (III) by the method used with I and II failed, owing probably to the formation of the phthalide. Attempts to obtain *p*-ClCH₂C₆H₄I (IV) by chlorination of *p*-MeC₆H₄I failed. It was obtained thus: *p*-MeC₆H₄NH₂ → *p*-MeC₆H₄I → *p*-ClCH₂BrC₆H₄I → *p*-HOCH₂C₆H₄I → IV, needles, m. 53-3.5°. *m*-Iodobenzyl chloride, m. 26.5-7.5°, was obtained similarly. *m*-Iodobenzyl bromide, m. 50-50.5°, was obtained by the bromination of *m*-MeC₆H₄I. *m*-IC₆H₄CH₂OH (V) was obtained, b_p 165° instead of 164, 151°, as previously reported in the literature. *o*-Iodobenzyl chloride, m. 28.5-9.5°, was obtained like IV. *o*-Iodobenzyl alc., m. 89.5-90°, was obtained like V. The data on the sapon. of these compds. are given in tables and are to be reviewed and discussed in connection with other data in another paper.

Platinum oxide as a catalyst in the reduction of organic compounds. III. Preparation and properties of the oxide of platinum obtained by the fusion of chloroplatinic acid with sodium nitrate. ROGER ADAMS AND R. L. SHRIVER, J. Am. Chem. Soc. 45, 2171-9(1923); cf. C. A. 17, 2277.—The reactions involved in the prepn. of the oxide are probably the following: 6NaNO₃ + H₂PtCl₆ → 6NaCl + Pt(NO₃)₄ + 2HNO₃; Pt(NO₃)₄ → PtO₂ + (NO₂)₂ + O₂. The fusion was carried out at various temps. between 310° and 700° and the products were tested as catalysts in the reduction of malic acid and BzH₂; that prep. at about 500° gave the best results. The oxide has the compn.

$\text{PtO}_2 \cdot 2\text{H}_2\text{O}$, is insol. in aqua regia, concd. HNO_3 and concd. HCl but readily sol. in HBr and in HCl contg. reducing agents (SO_2), decomps. H_2O_2 without itself being changed and oxidizes alcs. to the corresponding aldehydes. The nitrates of Li , K , Ca , Ba and Sr are not nearly as satisfactory as NaNO_3 for the prepn. of the oxide. This oxide is far superior as a catalyst to the various other oxides obtained by the methods given in the literature and, moreover, is much more readily prepd.

Synthesis of phenylanthranilic acids. NEAL, TUTTLE. *J. Am. Chem. Soc.*, **45**, 1906-16 (1923).—Three g. $o\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ (I), 2 g. $p\text{-H}_2\text{NC}_6\text{H}_4\text{NMe}_2$ (II), 3 g. K_2CO_3 and 2 g. Cu powder digested 2.25 hrs. in AmOH over a free flame give 3.1 g. *4'-dimethylaminodiphenylamine-2-carboxylic acid*, green, m. 216° (decompn.), converted at 220° into $p\text{-PhNHCH}_2\text{CH}_2\text{NMe}_2$, m. 130° ; heated 10 min. at 100° in concd. H_2SO_4 it gives 95% of *2-dimethylaminoacridone*, bright yellow, m. $289\text{--}90^\circ$. *4-Nitro-4'-dimethylaminodiphenylamine-2-carboxylic acid*, from II and $2,5\text{-Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{CO}_2\text{H}$ (III), Cu-colored, m. $234\text{--}5^\circ$ (yield, 75%). *2,4-Dinitro analog*, obtained in 100% yield from 1.6 g. II added dropwise to 3 g. $2,3,5\text{-Cl}(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{CO}_2\text{H}$ (IV) and 3.3 g. crystd. NaOAc in 20 cc. H_2O , bright yellow amorphous powder, m. 253° (decompn.); *HCl salt*, reddish brown, gradually m. $240\text{--}60^\circ$. *3'-Dimethylaminodiphenylamine-2-carboxylic acid*, from I and $m\text{-H}_2\text{NC}_6\text{H}_4\text{NMe}_2$ (V), m. 155° . *4-NO_2 deriv.*, from V and III, greenish brown, sinters and blackens without melting when slowly heated to 300° but melts sharply (decompn.) when dipped into a bath at 247° . *2,4-Di-NO_2 acid*, obtained in 3.9 g. yield from 3.7 g. IV and 2 g. V refluxed 35 min. in alc. and in 100% yield from 3 g. IV, 1.6 g. V and 3.3 g. crystd. NaOAc refluxed 1 hr. in H_2O , green, darkens above 300° ; *HCl salt*, green, sinters 320° . *4'-Diethylaminodiphenylamine-2-carboxylic acid*, from I and $p\text{-H}_2\text{NC}_6\text{H}_4\text{NEt}_2$ (VI), blue substance stable for 2 hrs. under its mother liquor at 0° but becomes gummy and black as soon as sepd. *4-NO_2 deriv.* (yield, 78%), brown, m. $239\text{--}40^\circ$. *2,4-Di-NO_2 compd.* (4 g. from 3 g. IV, 2 g. VI and 3.5 g. crystd. NaOAc boiled 5 min.), bright yellow, m. 259° ; *HCl salt*, orange, m. $252\text{--}3^\circ$. *3'-Diethylaminodiphenylamine-2-carboxylic acid*, from I and $m\text{-H}_2\text{NC}_6\text{H}_4\text{NEt}_2$ (VII), dark blue ppt. at once becoming black and gummy on the filter. With III, VII unexpectedly gives $[\text{4,2-O}_2\text{N}(\text{HO}_2\text{C})\text{-C}_6\text{H}_2]_2$, needles with 1 H_2O , m. (anhyd.) 257° . *3'-Diethylamino-2,4-dinitrodiphenylamine-6-carboxylic acid* (2 g. from 3 g. IV and 2 g. VII boiled 5 min. in 99% alc.), bright yellow, m. 220° (decompn.). With piperidine (VIII), Na_2CO_3 and Cu in AmOH I gives salicylic acid; that this is not due to the basic properties of the VIII is shown by the fact that when KOH is substituted for VIII, practically all the I is recovered unchanged. *2-Piperidino-5-nitrobenzoic acid*, from III and VIII, very pale yellow, m. $200\text{--}2^\circ$. Refluxed in H_2O with NaOAc and Cu, 3 g. IV and 1 g. VIII give 3 g. of $\text{Cu } 3,5\text{-dinitrosalicylate}$, green needles with 3 H_2O which is lost completely only at 180° , explodes violently at 320° . I refluxed with KOH in the presence or absence of Cu is recovered unchanged. In the 4 isomeric mono- NO_2 derivs. of I, the 3- NO_2 compd. has the most labile Cl atom, giving *2-nitrodiphenylamine-6-carboxylic acid*, yellow, m. 194° , when refluxed with PhNH_2 , K_2CO_3 and Cu in alc.; the 2nd acid, in order of the lability of the Cl, is apparently, as would be expected, the 6- NO_2 compd. (III), for, as shown above, the Cl is removed by bases at the temp. of boiling H_2O ; the 6- NO_2 acid digested with an excess of PhNH_2 in the presence of Cu chars completely, seeming to indicate that a NO_2 group in the 6-position makes the Cl less labile than in I.

Constitution of capsaicin, the pungent principle of capsicum. III. E. K. NELSON AND L. E. DAWSON. *J. Am. Chem. Soc.*, **45**, 2179-81 (1923); cf. *C. A.*, **14**, 1678.—*Hydrogenated capsaicin* (I), from capsaicin (II) in abs. alc. with H and colloidal Pd, m. 65° , n_D^{20} 1.510, 1.520, 1.555 for α , β and γ (the corresponding values for II are 1.520, 1.540, 1.580), does not decolorize Br in CHCl_3 , is also obtained by hydrogenating the decenoic acid (III) obtained from I, converting it into the chloride and condensing it with vanillylamine and is identical with *8-methylnonylvanillylamine*, similarly obtained from 8-methylnonoic acid (Levene and Allen, *C. A.*, **11**, 1414). I is as pungent as II, showing that a double bond is not necessary for pungency. Cold KMnO_4 oxidizes III to adipic and isobutyric acids, showing that II is $\Delta^8\text{-8-methylnonylvanillylamine}$, $4,3\text{-HO}(\text{MeO})\text{C}_6\text{H}_3\text{CH}_2\text{NHCO}(\text{CH}_2)_8\text{CH}:\text{CHCHMe}$.

4-Methoxyresorcyraldehyde from the roots of Decalepis Hamiltonii. M. G. SRINIVASA RAO AND M. SETHA IVENGAR. *Pagsumery Essent. Oil Record*, **14**, 300-1 (1923).—Expts. are described establishing the constitution of this natural product as 4-methoxyresorcyraldehyde. Attention is directed to the solid isolated by Goulding and Pelly (cf. *C. A.*, **2**, 1708), which S. and S. believe identical with the above.

Relation between molecular structure and odor in trisubstituted benzenes. I. Derivatives of *p*-methoxyacetophenone. M. T. BOGERT AND L. P. CURTIN. *J. Am.*

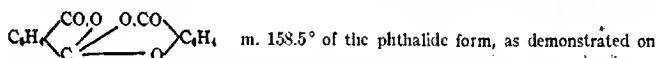
Chem. Soc. **45**, 2161-7 (1923).—So many well known perfume substances among the trisubstituted benzenes possess the 1,3,4-arrangement that this has been called the "ideal configuration." B. and C. have now made a no. of derivs. of 4-MeOC₆H₃COMe (I), a substance which itself has a fine floral odor, contg. an additional osmophore group in position 3, but all have been found to be practically odorless; a trisubstituted benzene contg. 3 osmophore groups in 1,3,4-relation is, therefore, not a perfume because of that, even though its phys. const. (b. p., solubilities, etc.) may be favorable. In carrying out reactions upon groups in the *o* position to the MeO group the well known obstacle of steric hindrance was encountered. As the result of their experience, B. and C. suggest the following hypotheses to supplement that of V. Meyer that the hindering effect of the interfering group increases with the mol. wt. The hindering effect of an interfering group diminishes (1) as the mol. wt. of the reacting group in the *o* position increases, and (2) as the mol. wt. of the foreign reacting mol. increases. The I, m. 38.9°, was obtained in 61% yield by a combination of the methods of Gattermann, Ehrhardt and Maisch and Charon and Zamanos. Na *p*-methoxyacetophenonesulfonate, from I and 4 parts fuming H₂SO₄ (30% SO₃) at 5°, fatty leaflets turning pink when exposed moist to direct sunlight, completely destroyed by fusing 3 min. with a low melting mixt. of NaOH and KOH; Me ester, from the Na salt with MeSO₃Na, 4,3-MeO(O₂NC₆H₃)COMe, obtained in 95% yield from I in concd. H₂SO₄ at 0° with HNO₃, H₂SO₄, lemon yellow, m. 99.5° (all m. ps. are cor.), gives with Sn and HCl 74% of the 3-NH₂ compd. (II), m. 102° (Ac deriv., m. 122.5°; benzal deriv., sirup solidifying only on long standing; *p*-nitrobenzal deriv., deep red to yellow, depending on the degree of subdivision, is hard and brittle at room temp., softens above 135°, m. completely 140°). 3-Iodo-1-methoxyacetophenone, obtained in 55% yield from II through the diazo compd., yellow, m. 103.6°, rapidly becomes brownish in the light, forms no phenol with boiling alc. KOH, gives in CHCl₃ with Cl a yellow 3-iodochloride which loses Cl so easily that it could not be obtained pure; in a closed vessel the Cl displaces H in the mol. and the only gas then found is HCl; with 5 M KOH the freshly pptd. iodochloride gives the 3-iodosa compd., grayish white, putty-like mass decomp. suddenly when heated; the alk. filtrate from this with SO₂ gives 3-iodoso-4-hydroxyacetophenone, pale yellow, m. 243° when heated cautiously but decomp. suddenly if heated rapidly. 3-Cyano-1-methoxyacetophenone (3-acetyl-1-methoxybenzonitrile), obtained in 70% yield from II by the Sandmeyer method, pale yellow, m. 159.5°, soon changes to light orange-yellow, is unchanged by alk. H₂O; hot 70% H₂SO₄ after several hrs. gives mainly tarry products with only a very small amt. of an acid, m. 255° (decompn.); boiling concd. HCl or hot 5 M KOH likewise failed to yield the acid. 2-Methoxy-5-acetyldiazobenzene perbromide, pale yellow, m. 68-70°, decomp. on standing or on heating in alc., seps. immediately and in almost quant. yield when the diazonium chloride is treated with the calcd. amt. of Br in HBr; in H₂O suspension with NH₄OH it instantly ppts. 2-methoxy-5-acetyldiazobenzene (yield, 75%), faint pinkish buff, darkens on standing, m. 87° (decompn.), explodes slightly above its m. p. when heated rapidly, forms a tar with hot 25% H₂SO₄. 2,2-Dimethoxy-5,5'-diacetyldiazoaminobenzene, obtained in 95% yield from II diazotized in HCl with the calcd. amt. of NaNO₂ and then treated with a 2nd equal amt. of II in HCl and finally with KOAc, pale yellow, m. 178°; allowed to stand 3 days in H₂O suspension with an equiv. amt. of HCl it yields mainly tarry products with a small amt. of the isomeric 4-aminoazobenzene, dark red, m. 198-200°, insol. in 10 M but sol. in 13 M HCl with greenish blue color. C. A. R.

Action of bromine on *p*-hydroxy- and *p*-methoxysulfonic acids. A. N. MELDRUM AND M. S. SHAH. *J. Chem. Soc.* **123**, 1982-6 (1923).—The reaction was carried out by passing 1 mol. Br. as vapor mixed with air, into the acid in H₂O. *p*-MeOC₆H₄SO₃H gave *p*-BrC₆H₄OMe, b. 216°. 2,5-MeO(SO₃H)₂C₆H₃Me (2.3 g.) and Br gave 1.8 g. 5-bromo-2-methoxytoluene, 6-sided plates with 1.5 H₂O, m. 71°, also obtained in 18 g. yield from 11 g. *o*-MeOC₆H₄Me. The action of Br upon 2,5-MeO(SO₃H)₂C₆H₃CO₂H or upon *o*-MeOC₆H₄CO₂H gave 2,5-(MeO)₂BrC₆H₃CO₂H, m. 121° (Peratoner. *Gazz. chim. ital.* **16**, 409), also prepd. by oxidizing 2,5-(MeO)₂BrC₆H₃Me with KMnO₄. If the bromination of the SO₃H deriv. is carried out at 0-5°, 50% conversion is secured and the remainder of the SO₃H deriv. recovered as the characteristic acid Na salt. In the case of the HO acids, a Br-SO₃H deriv. is obtained, the Br being in the *o*-position to the HO group. C. J. WEST

The constitution of sulfosalicylic acid and of related substances. A. N. MELDRUM AND M. S. SHAH. *J. Chem. Soc.* **123**, 1986-93 (1923); cf. Stewart, *C. A.* **17**, 545.—This work confirms the constitution as proved by Stewart. Pure HO(SO₃H)₂C₆H₃CO₂H is most conveniently prepd. by dissolving 100 g. HOC₆H₄CO₂H in 200 cc. H₂SO₄ contg. 3% SO₃, the temp. rising to 75°; crystn. set in after 0.5 hr.; the yield of crystd. acid was

160 g. The acid with 2 H₂O m. 113°, the anhyd. acid shrinks at 115° and decomps. about 180°. *Acid K salt*, needles with 3 H₂O (Mendius, *Ann.* 103, 45, states that it contains 2 H₂O). Br gives *3-bromo-5-sulfo-2-hydroxybenzoic acid*, needles with 0.5 H₂O, shrinks 110°, m. 140°, then solidifies and m. 182°. *Acid K salt*, needles with 2.5 H₂O. *Acid Na salt*, silky needles with 5 H₂O. *Ba salt* contains on rapid crystn. 1 H₂O, not lost at 100°, and on slow crystn. 5 H₂O, of which 4 are lost at 110°. *Sr salt*, needles with 1 H₂O, not lost at 110°. *Pb salt*, needles with 3 H₂O. The acid, heated with H₃PO₄ for a short time and then distd. with superheated steam (155-60°) gave 3,2-bis-(HO)C₆H₄CO₂H, m. 184.5° whose Ba salt is slightly red. With Me₂SO₄ this yielded *3-bromo-2-methoxybenzoic acid*, m. 136°, gives no color with FeCl₃. The Me ether of *o*-HOOC₆H₄CO₂H is readily scpd. by conversion into the Ca salt, the salt of the Me ether scgp. 1st, being much less sol. than Ca salicylate. *Sulfosalicylic acid Me ether*, m. 152°, was prepd. by sulfonation of *o*-MeOC₆H₄CO₂H, by methylation of *o*-HOOC₆H₄SO₃H and by oxidation of *o*-MeC₆H₄(SO₃H)Me. The *acid Na salt*, lustrous needles with 3 H₂O; *acid K salt*, needles with 2 H₂O; *Ba salt*, microneedles. The *salicyl chloride*, m. 148.5° and with NH₄OH gives the known amide, which with KOH (fusion) yields 2,5-HO(SO₂NH₂)C₆H₃CO₂H. This work establishes the constitution of Bromwell's acid (*Am. Chem. J.* 19, 569) as 2,5-MeO(SO₃H)C₆H₃Me. C. J. WEST

Substituted salicylic acids. II. H. P. KAUFMANN. *Ber. pharm. Ges.* 33, 120-32 (1923); cf. *C. A.* 16, 2321.—Phthalyl chloride (both sym. and asym.) and di-Na salicylate in equimol. proportions in CS₂ form *salicyl phthalidene ether-ester*,



application of the Pfeiffer quinhydrone test (cf. *C. A.* 13, 1471). Similarly, *5-bromo-salicyl phthalidene ether ester*, C₁₀H₅O₅Br, from sym. C₆H₄(COCl)₂ and *N*-5-bromosalicylic acid in C₆H₆, m. 176°; *3,5-dibromosalicyl phthalidene ether ester*, C₁₂H₅O₅Br₂, m. 217°; and *5-nitrososalicyl phthalidene ether ester*, C₁₂H₅O₅N, m. 214.5° were prepd. The latter yielded on reduction with Zn dust and AcOH in Et₂O *5-aminosalicyl phthalidene ether ester*, C₁₂H₇O₅N, which after coupling with PhNH₂ and β -naphthol yielded red- and



yields in C₆H₆ *o*-phthalyl disalicyl Et ester, C₂₈H₂₂O₈, m. 56°; with the Ph ester *o*-phthalyl disalicyl Ph ester, C₃₄H₂₂O₈, m. 112°; and with the β -naphthyl ester *o*-phthalyl disalicyl β -naphthyl ester, C₃₂H₂₀O₈, m. 78°, all the last 3 compds. being readily hydrolyzed by alkali, in contrast to the relative stability of salicylphthalidene ether ester in this respect. Of *p*- and *m*-C₆H₄(CO₂H)₂ derivs. the following were prepd. *Terephthalic disalicylic acid*, C₂₂H₁₄O₈, amorphous, decomp. 180-90° without melting; *Et ester*, C₂₈H₂₂O₈, m. 165°; *Ph ester*, C₃₄H₂₂O₈, needles, m. 189-90°; β -naphthyl ester, C₃₂H₂₀O₈, m. 80°. *Isophthalic disalicylic Et ester*, C₂₈H₂₂O₈, m. 90°; *Ph ester*, a non-solidifying and non-crystg. oil; β -naphthyl ester, C₃₂H₂₀O₈, m. 130°. W. O. E.

The tannin of tea. I. J. J. B. DEUSS. *Rec. trav. chim.* 42, 496-8 (1923).—Previous studies of the tannin of tea are reviewed by J. Dekker (*Die Gerbstoffe*, 1913). This study is being carried out parallel to that of the oxidizing enzymes (*C. A.* 17, 2428). When the tannin is prepd. by Nanninga's method (*Mededeel. land. Plantentuin* 46, 1, 23) a red product is also formed analogous to that obtained by the decompn. of tannin from oak. D. described a method of prepn. of tannin from tea yielding a white product which even when dry is oxidized in the air to a brown sirup. Analysis and mol. wt. detns. gave C₃₀H₂₀O₇ as the formula for this tannin (I). With FeCl₃ I gives a black ppt. and a blue-black coloration in very dil. solns.; with Pb(OAc)₂, a yellow-gray ppt.; with Br H₂O a yellow ppt.; KMnO₄ oxidizes it completely with the liberation of CO₂; with HNO₃ it gives H₂C₂O₄. It reduces Fehling soln., gives a yellow ppt. with PhNH-NH₂ and reduces Ag₂O-NH₄OH soln., which shows it contains a CO group. When boiled with 1:20 H₂SO₄ 6 hrs. it ppts. a red compd. similar to that obtained from oak tannin. I with Ac₂O + dry NaOAc gives the acetylated tannin, C₃₆H₂₀O₁₇, in which it is concluded that the H atoms of 8 phenolic OH groups are replaced by Ac. The results thus far obtained indicate that I contains at least 1 CO group, 8 OH groups and no CO₂H. E. J. WITZEMANN

Asymmetric dyes. C. W. PORTER AND H. K. IHRIG. *J. Am. Chem. Soc.* 45,

1990-3(1923).—The resolution of a racemic dye by the selective action of wool has been effected. *m*-Aminomandelic acid, m. 130° (decompn.), was obtained in 60% yield from the NO_2 acid with $\text{Ba}(\text{OH})_2$ and FeSO_4 at 30° and resolved through the cinchonine salts, m. 156.5°, into the *d*-acid, m. 130° (decompn.), $[\alpha]_D^{25}$ 33.80°, and the *l*-acid, m. 130° (decompn.), $[\alpha]_D^{25}$ -33.65°. The *d*-acid, diazotized at 0° and poured into cold alk. β -naphthol gives *d*-*m*- α - β -naphtholmandelic acid, m. 210°, $[\alpha]_D^{25}$ 49° ± 5°; *l*-isomer, similarly obtained, $[\alpha]_D^{25}$ -49° ± 5°. A typical dyeing expt. showing selective absorption is the following: 1 g. of the *dl*-dye in 75 cc. AcOH was treated with 2.5 g. wool at 20° for 24 hrs., when the filtered soln. showed a rotation of -0.66°; fresh wool was then added and after 48 hrs. the reading was -0.91°. In the course of this investigation the following additional compds. were prepd.: *p*-1,2- α - β -naphtholmandelic acid, bright red, insol. in acids, sol. in bases, m. 118°. *p*-Azoresorcinolmandelic acid, red., m. 154° (decompn.). *p*-Azodimethylanilinemandelic acid, brown, insol. in bases, sol. in acids, m. 125-9° (decompn.). *m*-Azoresorcinolmandelic acid, m. above 280°. *m*-Azodimethylanilinemandelic acid, reddish purple, m. 158°. *m*-Azophenolmandelic acid, bright yellow, m. 119°. β -Naphthalene- α -hydroxypropionophenone, from MgHBrCOBr condensed with AcNHPh , hydrolyzed, diazotized and coupled with β -naphthol, red, sol. in bases, insol. in acids, m. 132°. *Butyrophenone homolog*, red, m. 72°. *Isobutyrophenone compd.*, red, m. above 265°. C. A. R.

The addition of hydrogen to acetylenic acids. D. H. WILLIAMS AND T. C. JAMES. *Aberystwyth Studies* 4, 197-207(1922).—By reduction of $\text{PhC}(\text{CO}_2\text{H})_2$ with H in presence of colloidal Pt, Paal and Hartmann obtained *allo*-cinnamic acid (C. A. 4, 311) showing that *cis*-addn. had taken place. Expts. on the same lines with tetrolic acid have given similar results, 63% of the theoretical yield of *allo*-crotonic and only 4% of ordinary crotonic acid being obtained. Reduction of $(\text{C}(\text{CO}_2\text{H})_2)_2$ in the same manner, in the form of its normal K salt, gave, however, fumaric acid without any trace of maleic acid. The addn. thus takes place in the *trans*-position, and supports the views of Michael (C. A. 12, 908) on the relation between the energy content of such systems and their stereochem. activity. When $(\text{C}(\text{CO}_2\text{H})_2)_2$ is reduced with H and colloidal Pt in presence of less than 2 equivs. of alkali, the fumaric acid is further reduced to succinic acid almost as quickly as it is formed. J. C. S.

Cyclohexane-1,2-diol and *o*-chlorocyclohexanol. M. GOTCHHOFF. *Compt. rend.* 176, 448-50(1923); cf. *Compt. rend.* 175, 1411-14(1922).—*o*-Chlorocyclohexanol, prepd. by the action of monochloronitric in AcOH on cyclohexane, following the method of Detenof, b_p 84-5°, m. 29°. *Phenylurethan*, m. 97-8°. *Monooxalate*, b_p 122-4°, d₄ 1.091, n_D^{20} 1.4685, was prepd. by the action of AgOAc in AcOH. On sapon. with alc. KOH, this gave *trans*-cyclohexane-1,2-diol, m. 104°. A. C. PURDY.

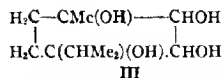
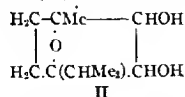
Some derivatives of 1,2-cyclohexanedione. SAMUEL COFFEY. *Rec. trav. chim.* 42, 528-32(1923).—The expts. here described constitute an attempt to obtain 1,2-cyclohexanedione (I). At first it was thought that if a compd. $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}_2\text{CO}_2\text{C}(\text{CHR})_2$ could be obtained by condensing cyclohexanone (II)

with a suitable aldehyde this on careful oxidation would give the desired diketone. Several aldehydes were condensed with II with $\text{EtOH}\cdot\text{HCl}$ and gave 2,6-di*p*-peronylidene-cyclohexanone, m. 187-8°; 2,6-di-*m*-nitrobenzylidene-cyclohexanone, m. 191-2°; 2,6-di*o*-anisylidene-cyclohexanone, m. 162°, giving a turbid liquid (liquid crystals) that clears at 172°. II apparently cannot form monobenzylidene derivs. in this way. Hydroxymethylencyclohexanone (III) (Borsche, C. A. 5, 463) was not used. III was freshly prepd. as the Na deriv., neutralized at 0° with dil. AcOH and added to PhN_2Cl soln. 1,2-Cyclohexanedione monophenylhydrazone (IV), m. 183-5°, was pptd. IV boiled with PhNHNH_2 in EtOH gave 1,2-cyclohexanedione osazone, m. 153-4°. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ acting upon IV in EtOH gave cyclohexanedione ketazine, 2,2'-diphenylhydrazone at once if the soln. was rendered acid, which gave striking confirmation of the results of Bruining (C. A. 17, 1963) on ketazine formation. Under the action of dil. acids derivs. like IV undergo "indole condensation," giving tetrahydrocarbazole derivs. (Borsche, C. A. 2, 1716; Perkin and Plant, C. A. 16, 421). 16 g. IV + 50 cc. glacial AcOH + 20 cc. concd. HCl boiled 30 mins. sepd. on cooling a brown solid from which 1-*ketotetrahydrocarbazole* (V), m. 169-70°, was sepd. With PhNHNH_2 V gave an oily phenylhydrazone. The oxime was obtained as a glassy mass. The oxime of V m. 228-30°. V heated to 70° with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ gave the ketazine, m. 258-60° (decompn.), which was the most characteristic deriv. of V obtained. The NH group in V could not be acetylated. BzCl even in the presence of Cu powder did not react with V. E. J. W.

Isomeric *l*-menthyl phenylchloroacetates. ALAN MCKENZIE AND ISOBEL A. SMITH. *J. Chem. Soc.* 123, 1962-78(1923).—Resolution of *l*-menthyl *dl*-phenylchloro-

acetate was effected by crystn. from EtOH at room temp. (low temps. appear to favor the sepn. of the partly racemic ester). The *d*-ester (I), m. 56-7°, is the less sol. In EtOH, ϵ 4.1732, $[\alpha]_D^{16.6}$ is 5.6°, $[\alpha]_{5461}^{16.6}$ 7.9°. The *l*-ester (II) m. 44.5-5.5° and in EtOH, ϵ 3.9912, shows $[\alpha]_D^{15}$ -149.8°. These esters were also prepd. by esterification of the active acids. A mixt. of the 2 esters in abs. Et₂O, after spontaneous evapn. of the solvent, gave the *dl*-ester, m. 28-9°, $[\alpha]_D^{18}$ -72.2°, $[\alpha]_{5461}^{18}$ -85.9° in EtOH, ϵ 3.9216. The transition temp. at which the partly racemic *r*-ester is transformed into the mixt. of equal quantities of the *dl*-esters has not been detd. but it would appear that this temp. lies below the ordinary. By the interaction of *l*-menthol and *dl*-PhCH₂COCl a *dl*-ester of practically the same properties was obtained (cf. Shimomura and Cohen, *C. A.* 16, 418). On resolution of this ester, the *d*-ester was found to be the more sparingly sol. (S. and C. report that the *l*-ester seps. 1st). Complete hydrolysis of I with EtOH-KOH at room temp. (1 week) gave a product, m. 56-73°, consisting chiefly of *r*-PhCHClCO₂H, but contg. some *l*-acid, since the rotation was $[\alpha]_D^{14}$ -1.3° (EtOH, ϵ 3.5372). In a 2nd expt. the rotation in C₆H₆, ϵ 5.598, was: $[\alpha]_D^{14}$ -3.0; $[\alpha]_{5461}^{14}$ -3.3°. Similar results were obtained on partial hydrolysis. The *l*-ester resembles the *d*-isomer in giving on hydrolysis an acid with a slight *l*-rotation, and an acid with practically the same rotation is obtained from the *dl*-ester (synthetic). This is explained by the fact that the velocity of formation of the *d*-ester is less than that of the *l*-ester, from which it can be shown that the *l*-acid (salt) will predominate at the end of the hydrolysis. In the fractional esterification of *r*-PhCHClCO₂H with *l*-menthol (Markwald and McKenzie, *Ber.* 32, 2130) the unesterified acid had $[\alpha]_D^{15}$ 4.3°. The action of SOCl₂ on *l*-menthyl *r*-mandelate gave a mixt. of 51% II and 49% I; with the *d*-ester, the proportions were 68% I and 32% II, while with the *l*-ester, the ratio was 30% I and 70% II. The action of PCl₅ upon the *d*-ester gave 81% I and 69% II, and upon the *l*-ester, 35% II and 65% I; the *r*-ester gave 48% I and 52% II. It is seen that although the 2 reagents are quite different in their behavior towards the diastereoisomeric esters, the final result of each action on the partly racemic ester is similar in that the product consists in each case of a mixt. of I and II with a slight preponderance of II. These expts. also present a type of Walden inversion but it is impossible to state at present which of the 2 reagents causes the configurative change. C. J. WEST

Oxidation of sabinene with hydrogen peroxide. G. G. HENDERSON and ALEXANDER ROBERTSON. *J. Chem. Soc.* 123, 1849-55 (1923).—Schmeller (*Ber.* 33, 1459) found that oxidation of sabinene (I) with KMnO₄ gave sabinene glycol and sabinenic acid. I in glacial AcOH is slowly oxidized by 30% aq. H₂O₂, yielding 2 isomeric glycol anhydrides, II, C₁₅H₂₄O(OH), an unstable acid and a little *p*-cymene. I (50 g.) and 84 g. 30% H₂O₂ in 200 g. AcOH were heated at 50-5° for 100 hrs. After neutralization with Na₂CO₃ and extrn. with Et₂O, a mixt. of II was obtained, best fractionated from Et₂O. II, m. 172°, crystals in needles and sublimes unchanged above its m. p. Its behavior with Br and KMnO₄ indicates that it is satd. and it does not form a semicarbazonc. *Mono-p*-nitrobenzoate, m. 176°. *Di-p*-nitrobenzoate, pale yellow, m. 192-3°. II, m. 174°, is more sol. than its isomer, and does not sublime; $[\alpha]_D^{25}$ 34.3° in EtOH. *Mono-p*-nitrobenzoate, m. 181-2°; *di*-deriv., m. 162-3°. Oxidation with KMnO₄ at 5° of the isomer, m. 172°, gave inactive HO₂CCMe(OH)CH₂CH₂C(OH)(CO₂H)CHMe₂, while the isomer, m. 174°, gave the active form of the same acid. A little HCO₂H was also formed in each case. The action of PCl₅ and HBr upon II gave unstable compds. From the mother liquor of II a small amt. of *p*-cymene was isolated by steam distn. A probable intermediate compd. in the formation of III is 1,2,3,4-tetrahydroxymenthane (III).



C. J. WEST

The reaction between α -pinene and acids. I. α -Pinene and sulfuric acid. KASHIUCHI ONO. *Mem. Col. Sci. Kyoto Imp. Univ.* 6, 305-11 (1923).— α -Pinene (I), shaken with H₂SO₄, yields terpin hydrate (II) and dipentene (III). The best yields of II are obtained from 100 g. I, 300 g. 45% H₂SO₄ at approx. 0° for 15 hrs. (83 g. II). Little II is formed with 10-30% H₂SO₄. Terpineol gives a quant. yield of II under the same conditions while dipentene also gives II (yield not stated). 100 g. turpentine oil, b. 155-60°, under these conditions gives 80 g. II. C. J. WEST

New halogen derivatives of camphor. III. α' , β - and α' , π -dibromocamphor. HENRY BURGESS AND T. M. LOWRY. *J. Chem. Soc.* 123, 1867-78 (1923); cf. C. A. 16, 2134.— α' , β - (I) and α' , π -dibromocamphor (II) have been prep'd. from the α , β - and α , π - isomers by adding alkali and then stabilizing the equil. mixt. by adding an acid. I was purified by crystn. from MeOH or better from AcMe. I m. 136°, $d_4^{25.7}$ 1.809, $[\alpha]_D$ -70.8°. In AcMe, c 5 g./100 cc., $[\alpha]_{589} = -85^\circ$; in EtOH, c 0.6 g./100 cc., -73°; in C₆H₆, c 16.14 g./100 cc., -83°. The α , β -isomer m. 111°, $d_4^{25.7}$ 1.825, $[\alpha]_D$ 82°; $[\alpha]_{589}$, in AcMe, c 5 g./100 cc., 127°, in EtOH, c 2.35 g./100 cc., 120°, in C₆H₆, c 16.23 g./100 cc., 101°. I belongs to the orthorhombic system; $a:b:c = 1.0117:1.01599$; forms present: $a(100)$, $b(010)$; $m(110)$, $p(210)$, $s(201)$, $t(201)$. The optical axial plane is parallel to $b(010)$, the acute bisectrix being parallel to $c(001)$. The angle $2V$ for Na light is 24° approx. The refractive indices are α 1.56, β 1.61 and γ 1.64. The study of mutarotation is rendered difficult because of the action of the alk. catalyst upon I, introducing a 3rd optically active component into the soln. The initial value of $[\alpha]_{589}$ in AcMe was -85.2° and with 0.01 N alkali, 95.5°. The α , β -deriv. gave 127° and 95.4°. This would indicate 9.8% I in the equil. mixt. Repetition of the measurements of the soly. and rotatory powers of sat'd. solns. of the α , β -deriv. confirmed the results reported in *J. Chem. Soc.* 89, 1033. II was 1st purified by crystn. from AcMe and was then repeatedly crystd. from EtOH. II m. 182°, $d_4^{25.2}$ 1.830, $[\alpha]_D$ 98.1°. The following values for $[\alpha]_{589}$ are reported for the 2 isomers (α' , π and α , π) (concn. in g./100 cc.): AcOH, c 1, 99°, 135°; AcOEt, c 5, 108.6°, 128.9°; EtOH, c 0.66, 109°, 128.1°; AcMe, c 5, 111.7°, 128.2°; CHCl₃, c 10, 118.6°, 125.9°; c 2, 119.5°, 126.1°; C₆H₆, c 5, 121°, 140.9°; PhMe, c 5, 120.9°, 108.4°; C₆H₆, c 5.63, 120.6°; c 11.75, 110.8°. The soly. of II in C₆H₆ and AcMe is about 6 g. per 100 cc., in cold MeOH or EtOH about 1 g. per 100 cc. II belongs to the orthorhombic system, $a:b:c = 0.9573:1.0442$; forms present $a(100)$, $b(010)$, $m(110)$, $s(201)$, $t(021)$. A soln. of 5 g. α , π deriv. in 100 cc. AcMe gave $[\alpha]_{589}$ 128.2° and after addn. of N/250 alkali 126.4°. Under the same conditions II gave 111.7° and 126.5°; the amt. of II present in the equil. mixt. is therefore 11%. The α' , α -deriv. had $d_4^{25.6}$ 1.854 and the α , π -deriv. $d_4^{25.2}$ 1.835. C. J. WEST

Camphor series. III. Catalytic action of reduced copper on d -camphoroxime. SHIGERU KOMATSU AND SHOZO YAMAGUCHI. *Mem. Col. Sci. Kyoto Imp. Univ.* 6, 245-50 (1923); cf. C. A. 17, 1455.—While camphoroxime with II in the presence of Ni gives bornylamine, in the presence of Cu and II the main reaction is a mol. rearrangement, with reduction as a side reaction. At 200° the reaction products are d - α -camphenolamide, α -camphenolic acid, d -camphor, α -camphenonitrile and a trace of bornylamine. Since the oxime yields the acid amide on rearrangement, a large part of it is the *syn*-form. C. J. WEST

Camphor and camphenilone series. S. S. NAMEKIN. *Ann.* 432, 207-31 (1923). (WITH A. M. KHUKHRUKOVA.) Penchone and MeMgI yield tert. methylcyclohexyl alc., which is dehydrated by K₂SO₄ to α -methylcamphene, m. 41-3°, b_{70} 170.5-1°. Heated with AcOH and 50% H₂SO₄ at 50-60° for 7 hrs., 6-methylisoborneol acetate, b_{70} 110°, d_4^{20} 0.9714, n_D 1.4634, $[\alpha]_D$ 18.85, results. This is quant. saponified by EtOH-KOH to 6-methylisoborneol (I), b_{70} 219-9.5°, m. 191-2°, $[\alpha]_D$ 14.8°. Phenylurethan, m. 101-2°. Acid phthalate, m. 167-8°. HNO₃ oxidizes I to 6-methylcamphor (II), b_{70} 213-3.5°, m. 168-8.5°. Semicarbazone, m. 251° (decompn.). Oxime, m. 131-2°. EtONa transforms II into 6-methylborneol, b. 219-20°, m. 183-4°. Phenylurethan, m. 108°; acid phthalate, m. 186°. Concd. KMnO₄ soln. oxidizes II to methylcamphoric acid (1,2,2,5-tetramethylcyclopentane-1,3-dicarboxylic acid), m. 185°, $[\alpha]_D$ 7.38°, 100 cc. H₂O at 22° dissolves 0.08 g. The anhydride, m. 206°, results by heating the acid to 250° or by heating with AcCl. (WITH M. SCHLESINGER.) *tert*-Methylbornyl alc., m. 153-5°, results by the action of MeMgI upon camphor. It is dehydrated by aq. AcOH, yielding α -methylcamphene. Dehydration of I by K₂SO₄ yields β -methylcamphene (III), b_{70} 170-70.5°, m. 100-1°. With AcOH and H₂SO₄ this yields the same ester as the α -deriv., and therefore on hydration gives I. The action of the N oxides from HNO₃ upon III in petrol. ether gives β -methylcamphenilone (3,3,6-trimethyl-1,7,4-dicyclohexanone-2) (IV), m. 141-2°. Semicarbazone, m. 231-2° (decompn.). Oxime, m. 172°. Hydrazone, b_{70} 245-7°, m. 85-7°. Azine, m. 163-4°. The hydrazone, heated with EtONa at 180-200°, gives β -methylcamphenilane, m. 116-7°. IV, reduced by EtONa, forms β -methylcamphenitol, m. 172-3°. PCl₅ gives a chloride and a hydrocarbon, which was not identified. Phenylurethan, m. 104-5°; acid phthalate, m. 174-5°. IV and NaNH₂ give β -methylcamphenilic amide, m. 124-5°. C. J. WEST

Chemical constituents of a Chinese drug "Hsiung-Ch'uang". II. YOSHIMARU MURAYAMA AND TAKEYOSHI ITAGAKI. *J. pharm. Soc. Japan* 1923, 143-8; cf. C. A. 16,

1578.—In addn. to the main constituent enidiolactone (*loc. cit.*), the volatile oils obtained by distg. the powd. drug with steam contains also a small quantity of sedanonic acid, m. 113° (the oxime, needles, m. 128°), and a sesquiterpene, a light yellow oil, b_p 110–20°, which gives a coloration changing from dark green to violet-red with Ac₂O and coned. H₂SO₄. J. C. S.

Isomerism of the dinitrobenzidines. O. L. BRADY AND G. P. McHUGH. *J. Chem. Soc.* 123, 2047–53 (1923).—Cain and co-workers (*C. A.* 7, 1356; 8, 1263, 3416) have shown that the dinitrobenzidines of Strakosch (*Ber.* 5, 236) (I) and of Bandrowski (*Monatsh.* 8, 471) (II) were different and ascribed to I the positions 3,5' for the NO₂ groups and to II the positions 3,3'. The constitution of I has been established by synthesis. 4-Iodo-2-nitrophenetole, orange-red, m. 80°, is obtained from 2,4-(O₂N)-(NHAc)C₆H₃ORt by heating with 20% H₂SO₄ until soln. results, then cooling, diazotizing and adding KI. With Cu powder at 185–95° for 40 min. and then at 215–20° for 20 min. this yields 3,5'-dinitro-4,4'-diethoxydiphenyl, m. 192–3°, also prepd. by the nitration of (EtOC₆H₄)₂. Heating in a sealed tube for 5 hrs. at 160–70° with EtOH-NH₃ gives I, m. 268°. The dinitrodiphenyls corresponding to I and II are best prepd. by adding 5 g. of I or II to a mixt. of 125 cc. abs. EtOH and 50 cc. fuming H₂SO₄ (20% SO₃), heating on a H₂O bath and adding 15 g. powdered NaNO₂ in small portions. Reduction of these with SnCl₄ and HCl yielded the 3,3',4,4'- and 3,5',4,4'-tetraaminodiphenyls, analyzed as the HCl salts. Differences in the behavior on crystn. and examn. of the crystals indicated that the salts were quite distinct. Both salts give the same diquinoxaline deriv. as stated by Cain. With HNO₃ the 3,5',4,4'-deriv. gives a diphenyldiazoinide, previously described by Brunner and Witt (*Ber.* 20, 1024), but the isomer gives a brownish red amorphous substance, C₁₂H₁₀O₂N₄(?). Other attempts to interconvert I and II or their derivs. failed. C. J. WEST

Molecular configuration of polynuclear aromatic compounds. IV. 6,6'-Dichlorodiphenic acid; its synthesis and resolution into optically active components. G. H. CHRISTIE, C. W. JAMES AND JAMES KENNER. *J. Chem. Soc.* 123, 1948–51 (1923); cf. *C. A.* 17, 2282.—2-Iodoaceto-*m*-toluidide is oxidized by KMnO₄ in boiling H₂O contg. MgSO₄ to 2-iodo-3-acetylaminobenzoic acid, m. 199°. Hydrolysis with coned. HCl gives the HCl salt of 2-iodo-3-aminobenzoic acid, m. 262–3°. 3-Chloro-2-iodobenzoic acid, m. 137–8°; Me ester, b_p 182°; Et ester, b_p 175°. The Me ester and Cu powder, heated 1 hr. at 230–40°, give 6,6'-dichlorodiphenic acid, m. 288°, as the Me ester, m. 156°. Et ester, m. 103–4°. Repeated fractional crystn. of the mixt. of salts from 2 g. acid and 6 g. hydrated brucine gave 2.3 g. of brucine 1-6,6'-dichlorodiphenate, C₁₂H₈O₄·N₄Cl₂·3H₂O, m. 235°, and is the less sol. of the 2 salts. $[\alpha]_D^{15}$ 1.97 (CHCl₃, c 1.23%). The *d*-salt, obtained in a yield of 1.35 g., m. 163° (decompn.), is the more sol. and has $[\alpha]_D^{15}$ –58.62° (CHCl₃, c 1.16%). This salt crysts. with 1.5 H₂O. *d*-6,6'-Dichlorodiphenic acid, m. 259°. A 0.69% soln. of the Na salt showed $[\alpha]_D^{15}$ –20.18°. The *l*-acid m. 259°; a 1.01% aq. soln. of the Na salt showed $[\alpha]_D^{15}$ 21.43°. These results confirm the correctness of the assumption that the cause of the stereoisomerism of the various nitrodiphenic acids previously investigated is not to be sought in any peculiar property of the NO₂ group. C. J. WEST

The reactions of esters with organomagnesium derivatives. V. G. L. STADNIKOV. *J. Russ. Phys. Chem. Soc.* 48, 1870–4 (1916); cf. *C. A.* 8, 3660; 10, 1355; 11, 582.—HCO₂Et is allowed to react with PhMgBr in the presence of a small quantity of I. The products of this reaction are Ph·CHOEt and (Ph₂CH)₂O. The formation of these substances is due to the formation of some Ph₂CHI, which reacts with the EtOMgBr produced in the first part of the reaction giving the mixed ether, or with Ph₂CHOMgBr to give the simple ether. The formation of Ph₂CHI as an intermediate product of the reaction is proved by the formation of (Ph₂CH)₂ in the following reaction. Ph₂CHOMgI is prepd. from excess of Mg, benzohydrol, and I, HCO₂Et is added, and the soln. boiled. A no. of tarry products are formed, from which (Ph₂CH)₂ (formed by the elimination of I from two mols. of Ph₂CHI) is sep'd. The reaction between α-C₁₀H₇MgBr and HCO₂Et gave a quantity of tarry matter from which some (α-C₁₀H₇)₂CHOEt is isolated. This is formed in the same way as the corresponding diphenyl substance in the previous expt. J. C. S.

The reactions of iodomagnesium alkyl oxides with esters. II. G. L. STADNIKOV. *J. Russ. Phys. Chem. Soc.* 48, 1875–81 (1916); cf. *C. A.* 9, 3051.—Iodomagnesium menthyl oxide is formed by the action of menthol on MeMgI, and an excess of HCO₂Et is added. After boiling for 20 hrs., menthyl formate is sep'd. from the reaction mixt. Iodomagnesium triphenylcarbinyl oxide is prep'd. from Ph₃COH and MeMgI. To this HCO₂Et and a little I are added, and the mixt. is boiled for 40 hrs. A variety of

products results, from which $(\text{Ph}_2\text{C})_2\text{O}_2$ is isolated, produced by the action of atm. O on the C_6Ph_2 formed by the elimination of I from two mols. of Ph_2Cl . A larger yield of the peroxide is obtained by repeating the previous reaction in the presence of excess of Mg and at the same time some Ph_2COEt is formed. Iodomagnesium benzo-hydryl oxide is prepd. by the action of benzhydrol on MeMgI , and is boiled for 30 hrs. with HCO_2Et . In the reaction products, $(\text{Ph}_2\text{CH})_2$, formed from 2 mols. of Ph_2CHI by the elimination of I, is found, together with $(\text{Ph}_2\text{CH})_2\text{O}$ and Ph_2CHOEt , formed by the interaction of EtOMgI with $\text{HCO}_2\text{CHPh}_2$. On repeating this reaction, using an excess of Mg, an increased yield of $(\text{Ph}_2\text{CH})_2$ is obtained, proving that Ph_2CHI is an intermediate product in the formation of the ethers. The same reaction was repeated with AcOEt instead of HCO_2Et , and resulted in the production of $(\text{Ph}_2\text{CH})_2$ and of a quantity of tarry matter from which no identifiable product was isolated. J. C. S.

The action of alcoholic potash on ketones. VIII. The substitutibility of bromine atoms by hydrogen in bromobenzophenones and their derivatives. P. J. MONTAGNE, *Rec. trav. chim.*, **42**, 499-510 (1923).—Earlier investigations have shown that in the action of EtOH-KOH on $\text{BrC}_6\text{H}_4\text{COPh}$ not only is the CO group reduced to CHOH but the Br atom is more or less substituted by H. The greater or less completeness with which the Br is substituted depends on the position of the Br atom with respect to the CO group. Since an *o*-Br atom is more easily replaced than a *m*- or *p*-Br atom (C. A., 7, 1178), it might be concluded that this Br atom is less firmly bound than the others. That this is not true was shown by the fact that none of the Br in $\text{BrC}_6\text{H}_4\text{CH(OH)Ph}$ is removed by boiling with EtOH-KOH . Consequently the Br is replaced before reduction takes place; when the reduction is complete no more Br is replaced. M. then reviews and discusses later work on the same topic (C. A., 11, 1176; 17, 1959). The intermediate transformation of $\text{BrC}_6\text{H}_4\text{COPh}$ into COPh is so far an unproved assumption. In this paper M. sought for a deriv. in which the velocity of reduction of the debrominated deriv. is slow enough to permit of its isolation owing to the retarding effect of another substituent upon the reduction reaction. This result was obtained with 3,5,4- $\text{Br}_2(\text{H}_2\text{N})\text{C}_6\text{H}_2\text{COPh}$ (D). In this compd. the retarding influence of the NH_2 upon the reduction is rendered almost ineffective by the 2 Br atoms. After boiling I 2 days with EtOH-KOH it was still partially unchanged. If 1 Br atom is replaced with H the 1-amino-3-bromobenzophenone (II) may be boiled 2 days with EtOH-KOH without being changed. When I is boiled with EtOH-KOH 2 days 3,5,4- $\text{Br}_2(\text{H}_2\text{N})\text{C}_6\text{H}_2\text{CH(OH)Ph}$ (III) and II are formed. From this it is concluded that 2 reactions take place simultaneously: (1) in part of I the reduction of CO to CHOH takes place; (2) in another portion Br is replaced by H. 2-Bromo-4'-hydroxybenzophenone (IV) remains almost entirely unchanged when heated with EtOH-KOH for 2 days, and no 4-HOC₆H₄COPh could be obtained. The small amt. of KBr formed is thought to be due to a side reaction. The mechanism of this Br substitution is discussed in detail in terms of an addn. of EtOH to the affinity residues of the C-Br group in which the C-Br union is relaxed with the increase of the C-H union involving the same C atom. An improved method for prep. 4-H₂NC₆H₄COPh (V) by treating 4-O₂NC₆H₄COPh in boiling EtOH with SnCl_4 in HCl is described. V boiled 2 days with EtOH-KOH remained unchanged (C. A., 7, 1178). 28 g. V in 375 cc. AcOH were treated with 7 cc. Br_2 in 75 cc. AcOH ; some II, *b_p* 241°, *m.* 157.75°, sepd. at once. The constitution of II was detd. by diazotizing it and converting it into 3-BrC₆H₄COPh, *m.* 77°. II remained unchanged after boiling 2 days with EtOH-KOH . III was also recovered unchanged. 50 g. 2-bromo-4'-ethoxybenzophenone (C. A., 15, 64) in 500 cc. AcOH + 500 cc. HBr (d. 1.49) were boiled 2 days, H_2O was then added and most of the AcOH and HBr evapd. on the H_2O bath. The ppt. formed on again adding H_2O was dissolved in KOH and IV was pptd. by adding AcOH ; it *m.* 100-5° if heated slowly, otherwise *m.* 114°. IV was unchanged by the action of EtOH-KOH .

E. J. WITZEMANN

Absorption spectra and chemical constitution of organic compounds. E. C. C. BALY, I. M. HEILBRON AND A. W. STEWART, *Rept. Brit. Assoc. Adv. Sci.*, **1922**, 294-315.—The original hypothesis of a direct correlation between the absorption bands shown by a substance in the visible and ultra-violet region of the spectrum and the constitution of that compd. has been proved to be untenable. In the report for 1920, a theory was put forward, based on the energy quantum theory, which gives an explanation of the phenomenon. Four initial assumptions are made: Every elementary atom is characterized by a definite quantity of energy associated with a definite phys. process taking place within itself. (2) The electron shift occupies a definite period of time, which is the same for all atoms. (3) When atoms unite to form a mol. energy is lost in the process and it is assumed that each of the two atoms contributes 0.5 of

the total energy lost when the 2 combine. (4) The at. quanta of all atoms are integral multiples of a fundamental unit of energy. The most important facts emphasized are the characterization of a mol. by its own mol. quantum and the possibility of a mol. gaining an amt. of energy equal to its characteristic quantum on exposure to radiation of frequencies equal to those of its atoms or component groups of atoms. In addn. to the mol. quantum, the mol. is characterized by the at. quanta, intra-mol. quanta and phase quantum, which is an integral multiple of its mol. quantum. The particular phase into which a freshly synthesized mol. will pass when in the free state depends upon 2 factors, the relation between the external force fields of its atoms and the temp. (long-wave radiations). A phase change may also be brought about by any method of supplying energy to the mol., such as exposing them to short-wave radiation of frequency equal to their phase frequencies and by the action of a solvent or catalyst. These are discussed and illustrated by examples. The 2nd part of the report consists of a brief account of the application of mol. phases to chem. reactions. The phenomenon of photocatalysis and its applications afford the strongest evidence yet found for the theory of mol. phases.

C. J. WEST
The structure of phenolphthalein oxime. W. R. ORNDORFF AND S. T. YANG. *J. Am. Chem. Soc.* 45, 1926-33(1923).—In order to explain the quant. decompn. of phenolphthalein oxime (I) by dil. H_2SO_4 into α -(p - HOC_6H_4CO) $C_6H_4CO_2H$ (II) and p - $H_2NC_6H_4OH$, I was assigned the structure $(HOC_6H_4)_2C_6H_4CO.NOH$ (C. A. 11, 1828).

It was further assumed that, like the oximes of the ketones, it undergoes the Beckmann rearrangement, forming an intermediate product, $HOC_6H_4C(OH).C_6H_4CO.NC_6H_4OH$

(III), which then hydrolyzes into the compds. above. These assumptions have now been verified experimentally. Meyer and Kissen's "triacetate of I" (*Monatsh.* 17, 440 (1896)), m. 235° (M. and K., 229-30°), is colorless while I itself is yellow, and it is really the triacetate of III; cold concd. H_2SO_4 or dil. NaOH hydrolyzes it to III, crystals with 1.5 H_2O , m. 135° (decompn.), which at 95° in CO_2 lose 2.5 mols. H_2O , yielding a dark red liquid, solidifying to a dark red glass, $O:C_6H_4:C_6H_4CO.NC_6H_4OH$ (IV). IV is very difficultly sol. in hot H_2O , but very

sol. in dil. alkalis with dark green color, acids giving a yellow amorphous ppt. When recrystd. from different org. solvents, III shows different m. ps. (94-5° from Me_2CO , 125° from $MeOH$, 130° from $EtOH$, 195-8° from $AcOEt$; this last prepn. seems to contain 0.5 mol. $AcOEt$). III behaves just like I towards boiling dil. H_2SO_4 , concd. $NH_4OH.HCl$, Zn dust and H_2SO_4 in alc., Ac_2O and $NaOAc$ and $BzCl$ and NaOH; in the last case, however, the product is a dibenzoate, $C_{20}H_{13}O_4NBz_2$, m. 227°, while M. and K. claim to have obtained (from I) a tribenzoate, m. 175°. With alk. Me_2SO , I gives Meyer and Spengler's yellow tri-Me ether of I, m. 145-6° (*Ber.* 36, 2961(1903)), while III gives a colorless tri-Me ether, m. 131-3°, showing that in the alkylation I does not undergo the Beckmann rearrangement. Attempts to synthesize III by melting II and p - $H_2NC_6H_4OH$ together resulted in the formation of a dark purple solid sol. in alkalis with deep purple color and repptd. by acids; it is probably a mixed phthalcin, $HO_2CC_6H_4C(C_6H_4OH):C_6H_4(NH_2):O$. C. A. R.

Chromoisomerism in the stilbene series. N. M. CULLINAN. *J. Chem. Soc.* 123, 2053-60(1923).—The general method of prepn. of the stilbene compds. was the condensation, in the presence of piperidine, of nitrotoluenes and aromatic aldehydes. In the case of the $O_2NC_6H_4Me$, no reaction occurred and the $O_2NC_6H_4CO_2H$ were used. 4-Nitro-4'-hydroxystilbene crystals from glacial $AcOH$ or better dil. $EtOH$ in bright yellow leaves, m. 204°. On addn. of petrol. ether to a cold dil. C_6H_6 soln., a greenish yellow modification was obtained, readily changed to the yellow form on being rubbed or heated. From a concd. $EtOH$ soln. black needles of $C_{14}H_{11}O_2N.2EtOH$, m. 158°, sep'd. on pouring a hot concd. $EtOH$ soln. into a little H_2O , a red powder, $C_{14}H_{11}O_2N.EtOH$ sep'd., changing to yellow at 100°. The *Ac* deriv., m. 182-4°, is yellow and exists only in I form. The concd. H_2SO_4 soln. is intensely violet. 2,4-Dinitro-4'-hydroxystilbene is obtained in large deep red prisms from a concd. soln. in glacial $AcOH$ (stable form) and as deep yellow needles on pouring the $AcOH$ soln. into H_2O . At 100° its color changed to red. Both forms give the same color in soln. 4-Nitro-2'-acetoxy-stilbene, bright yellow, m. 135°, is a by-product of the prepn. of 3-p-nitrophenylcoumarin from p - $O_2NC_6H_4CO_2H$ and o - HOC_6H_4CHO . 2,4,6-Trinitro-2'-hydroxystilbene, yellow, m. 148°. 4-Nitro-3'-hydroxystilbene, bright yellow, m. 188°, results from p - $O_2NC_6H_4CO_2H$ and m - HOC_6H_4CHO . 2,4-Dinitro deriv., yellow, m. 194°. 2,4,6-Trinitro deriv., yellow, m. 205°. 3-Nitro-4'-hydroxystilbene, m. 210°, from m - O_2N -

$\text{C}_6\text{H}_4\text{CO}_2\text{H}$ and $p\text{-HOC}_6\text{H}_4\text{CHO}$, *3-m-Nitrophenylcoumarin*, m. 251° , from $m\text{-O-N-C}_6\text{H}_4\text{CO}_2\text{H}$ and $a\text{-HOC}_6\text{H}_4\text{CHO}$, *4,4'-Dinitrostilbene*, pale yellow, m. 231.5° , from $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ (Walden and Kernbaum, *Ber.* 23, 1959, give the m. p. as $210\text{--}6^\circ$). *4,3'-Dinitrostilbene*, yellow, m. 155° . The solids in EtOH, CHCl_3 , C_6H_6 or AcMe are green. The colors of the above compds. in C_6H_6 , glacial AcOH and $\text{CH}_3\text{CO}_2\text{H}$ are given; they vary considerably with the nature of the solvent. The differences are evidently due to the formation of additive compds. C. I. West

Spontaneous dissociation of triphenylmethyl disulfide with the formation of triphenylmethyl. The potassium derivative of triphenylcarbinol and its use as a synthetic agent. F. F. BLICKER, *J. Am. Chem. Soc.* 45, 1965 9(1923); cf. C. I. 17, 1176. Solns. of $(\text{Ph}_3\text{C})_2\text{S}_2$ in dry C_6H_6 immediately assume the deep yellow color of PhC and when air is passed through the soln. and then into aq. KOH $(\text{Ph}_3\text{C})_2\text{O}_2$ is pptd. and K_2SO_3 is found in the KOH, showing that SO_2 is also formed during the reaction. As shown by Wieland (C. I. 5, 3821) $(\text{Ph}_3\text{C})_2\text{O}_2$ also dissociates very readily in boiling xylene, but in this case the dissociation occurs, not between the PhC group and the O but between the two O atoms. It seemed desirable therefore to prep. the unknown thioperoxide, $\text{Ph}_3\text{COSCPh}_3$, which it was thought might be made from Ph_3CSCl and a metallic deriv. of PhCOH. Ph_3CSCl refluxed 1.5 hrs. with K in xylene in a N atm. yields the K salt, KOCPh_3 , in transparent crystals losing about 21% xylene at 220° under 20 mm. and changing to an opaque granular mass; in air the crystals quickly change to a powder; in the presence of moisture they give PhCOH and KOH. Refluxed in C_6H_6 with MeI, the K salt gives 82% Ph_3COMe , m. 83.1° , with EtI in boiling C_6H_6 it reacts according to the equation $\text{Ph}_3\text{COK} + \text{EtI} \rightarrow \text{Ph}_3\text{COH} + \text{C}_6\text{H}_5\text{I} + \text{KI}$; with BzCl in C_6H_6 it immediately forms Ph_3COBz , m. 165.6° . With Ph_3CCl in C_6H_6 it evolves heat and forms a red-brown soln. but the only cryst. org. compds. that could be isolated were Ph_3COH and $(\text{Ph}_3\text{C})_2\text{O}_2$; since considerable amts. of KCl were formed, it seems that $\text{Ph}_3\text{COSCPh}_3$ must have been formed initially and the $(\text{Ph}_3\text{C})_2\text{O}_2$ may have resulted from the interaction of the thioperoxide with unchanged Ph_3COK . With Ph_3CCl , Ph_3COK yields $p\text{-HOC}_6\text{H}_4\text{CPh}_3\text{OH}$, probably present in the reaction mixt. as the anhydride, $\text{Ph}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{O}$. Ph_3COK reacts at once with I, PCl_5 and other substances with reactive halogen. C. A. R.

The mechanism underlying the reaction between aldehydes or ketones and tautomeric substances of the keto-enol type. E. P. KOHLER AND B. B. CORSON, *J. Am. Chem. Soc.* 45, 1975-86(1923).— BzCO_2Me , which cannot enolize, condenses with $\text{NC-CH}_2\text{CO}_2\text{Me}$ under the influence of NaOMe , NH_3 , MeNH_2 , PhNH_2 , and piperidine in the same way and almost with the same ease as aldehydes, forming the unsatd. compd. $\text{PhC}(\text{CO}_2\text{Me})\text{:C}(\text{CN})\text{CO}_2\text{Me}$ (I); with the same condensing agents but under different conditions it is possible to obtain as the principal product the satd. compd. $\text{PhC}(\text{OH})_2(\text{CO}_2\text{Me})\text{C}(\text{CN})\text{CO}_2\text{Me}$ (II). There remains no reason for assuming, therefore, that either the reaction between aldehydes or ketones and substances which have active H or aldol condensation involves the enolization of aldehydes or ketones. II is a stable substance; when perfectly pure it neither readily loses H_2O nor reverts to its components. Thus, in pure boiling MeOH or Me $_2\text{CO}$ it has a normal mol. wt. and the solns. can be boiled for hrs. without a change in the mol. wt. Heated under very low pressures it partly distils and partly dissociates into its components. Efficient dehydrating agents, however, eliminate H_2O ; heated with PCl_5 in POCl_3 or in glacial AcOH II smoothly passes into I. Since no I is formed when an equimol. mixt. of the 2 components is treated in the same way, it must here be formed by loss of H_2O from II. II is exceedingly sensitive to bases, disappearing more or less completely in the presence of any of the condensing agents used in its synthesis. Thus, in boiling MeOH or Me $_2\text{CO}$ contg. relatively very small amts. of any of these bases the b. p. of the soln. rapidly rises and finally reaches a const. temp. corresponding to a mol. wt. much lower than that calcd. for II; the soln. now contains $\text{CH}_2(\text{CO}_2\text{Me})_2$ and BzCO_2Me as well as II, but no I can be isolated from it. When solns. of II contg. larger amts. of the bases are boiled or, better, when the solid II, suspended in a little of the solvent contg. a small amt. of base, is kept at room temp., it gradually changes into I. The basic condensing agents constantly employed in the synthesis of α,β -unsatd. compds. fulfil a 2-fold function: they bring about condensation and they cause the elimination of H_2O . There is, however, at present no proof that II is an intermediate product in the formation of I; inasmuch as II in the presence of bases reverts to an equil. with its components, it is impossible, in the absence of all accurate knowledge of the kinetics of the reaction, to det. whether I is formed by loss of H_2O from II or directly from the components in some other way. There is nothing peculiar in the above condensation with $\text{NC-CH}_2\text{CO}_2\text{Me}$. $\text{CH}_2(\text{CO}_2\text{Me})_2$ behaves in precisely the same way; the addn. product is

less sol. and therefore a little more easily isolated; the residual H in the $\text{CH}(\text{CO}_2\text{Me})_2$ residue is less active than that in the $\text{CH}(\text{CN})\text{CO}_2\text{Me}$ residue and the addn. product loses H_2O less readily, and moreover, as the resulting unsatd. compd. is a liquid, it is more difficult to get it as a direct product of the condensation. When an equimol. mixt. of BzCO_2Me and $\text{NCCH}_2\text{CO}_2\text{Me}$ at 0° is treated with a few drops of a satd. soln. of NaOMe in MeOH (or with a small amt. of NH_3 , MeNH_2 or piperidine) the liquid changes in 5-10 min. to a solid contg. 75-80% II, the amt. of which does not increase on further standing for several hrs. The equil. $\text{BzCO}_2\text{Me} + \text{NCCH}_2\text{CO}_2\text{Me} \rightleftharpoons \text{II}$ is shifted to the left by dilg. the mixt. with a solvent but this can be counteracted by lowering the temp.; thus, in an equal vol. of MeOH at -20° the crude product still contains 72.5% II. The *di-Me* α -phenyl- α -cyano- β -hydroxysuccinate (II) is best isolated by thoroughly mixing the cold crude product with AcCl , filtering, washing with cold AcCl dild. with Et_2O and finally very thoroughly with H_2O , drying, digesting several hrs. with AcCl and recrystg. from CHCl_3 contg. a little PCl_5 ; it then m. 155° . *Di-Me* α -phenyl- β -cyanoethylendicarboxylate (I), obtained in 70-5% yield from BzCO_2Me and $\text{NCCH}_2\text{CO}_2\text{Me}$ with NaOMe in boiling MeOH or with $\text{MeNH}_2\cdot\text{HCl}$ and Na_2CO_3 in a little MeOH at room temp. or from II in MeOH with NaOMe or in hot AcOH , m. $79-80^\circ$, reduces KMnO_4 in Me_2CO with great ease. A satd. soln. of KOH in MeOH hydrolyzes I at room temp. to α -cyano- β -phenylmaleic acid (III), very pale yellow; acid K salt, m. $193-5^\circ$; anhydride, obtained by heating the acid, yellow, m. $145-6^\circ$. All attempts to hydrolyze I or III to the corresponding tribasic acid failed; hot coned. aq. alkalis produced a free evolution of NH_3 but the chief product was BzCO_2H . The CN group in I is just as resistant to acids; I is recovered almost completely unchanged from a dry MeOH soln. satd. with HCl and allowed to stand 3 days or heated 27 hrs. in an autoclave; 10 g. heated 3 hrs. on the H_2O bath and 5 min. to boiling with 10 g. AcOH and 20 cc. concd. H_2SO_4 yielded 3 g. α -cyano- β -phenylsuccinic acid, plates with $2\text{H}_2\text{O}$, m. (anhyd.) $158-60^\circ$ (decompn.), sublimes unchanged *in vacuo*. The di-K salt of III in H_2O with a 30% excess of 2% Na-Hg gives $\text{PhCH}(\text{CO}_2\text{H})\text{CH}(\text{CH}_2\text{NH}_2)\text{CO}_2\text{H}$ and an acid m. $168-9^\circ$ and having the compn. $\text{PhCH}(\text{CO}_2\text{H})\text{CH}(\text{CH}_2\text{NH}_2)\text{CO}_2\text{H}$. When the Na-Hg was added rapidly and the product obtained by acidifying with HCl and extg. with Et_2O was esterified in MeOH with HCl there was obtained *tri-Me* phenyl-ethanetricarboxylate, m. $107-8^\circ$. *Tri-Me* β -phenyl- β -hydroxyethylane- α,α,β -tricarboxylate, prepd. like II from BzCO_2Me and $\text{CH}_2(\text{CO}_2\text{Me})_2$ (yield, about 80%), m. $109-11^\circ$, mol. wt. in freezing AcOH 301, is so sensitive to bases that the b. p. of a soln. in MeOH which had been distd. from lime rose steadily for 0.5 hr. when it became const. at a temp. corresponding to a mol. wt. of 215. Similar results were obtained in carefully purified Me_2CO but when the latter was previously refluxed with tartaric acid and the ester was crystd. from Et_2O which had been washed with H_2SO_4 , the b. p. became const. in 4 min. at a temp. corresponding to a mol. wt. of 274. Heated in a sealed tube with POCl_3 and a little more than 1 equiv. PCl_5 the satd. ester yields *tri-Me* β -phenylethylene- α,α,β -tricarboxylate, oil, most of which b.p. $180-90^\circ$, hydrolyzed by cold concd. KOH to a liquid acid which is reduced by Na-Hg to $\text{PhCH}(\text{CO}_2\text{H})\text{CH}(\text{CO}_2\text{H})_2$, m. 190° . C. A. R.

Reaction between cyanoacetic esters and benzalacetone. E. P. KOHLER AND PAUL ALLEN, JR. *J. Am. Chem. Soc.* **45**, 1987-90(1923).—Haworth by condensation of $\text{PhCH}:\text{CHCOMe}$ with $\text{NCCH}_2\text{CO}_2\text{Et}$ obtained an unsatd. acid m. 188° to which he assigned the structure $\text{PhCH}:\text{CHCOMe}:\text{C}(\text{CN})\text{CO}_2\text{H}$ (C. A. **3**, 2123), while Vorländer by almost exactly the same method had previously obtained an acid m. 180° which he showed pretty conclusively to have the structure $\text{PhCH}:\text{CH}(\text{CN})\text{CO}_2\text{H}$.

(I) (*Ann.* **294**, 253(1897)). Repetition of the work of these 2 investigators has shown that V. is correct, I being formed according to the scheme $\text{PhCH}:\text{CHCOMe} + \text{NCCH}_2\text{CO}_2\text{Me} \rightleftharpoons \text{PhCH}(\text{CH}_2\text{COMe})\text{CH}(\text{CN})\text{CO}_2\text{Me}$ (II) \rightarrow I. The first step of the reaction is reversible and in the presence of the large amts. of Na alcoholate used by V. and by H. the concn. of II is always small, but when the amt. of condensing agent is reduced to a trace there is no difficulty in isolating II, the process being exactly the same as that discussed in the preceding abstr. I, obtained in 26.5% yield by the method of V. and of H., m. 180° ; Me ether, from I in MeOH with dry HCl , m. $171-2^\circ$. With KMnO_4 in Na_2CO_3 I is oxidized to $\text{HO}_2\text{CCHPhCH}_2\text{CO}_2\text{H}$, m. 165° . From 27.5 g. each of $\text{PhCH}:\text{CHCOMe}$ and $\text{NCCH}_2\text{CO}_2\text{Me}$ treated dropwise with 5% NaOMe until alk. to litmus and boiled 12 hrs. with addn. of NaOMe as required to maintain the alkalinity is obtained 32.5 g. *Me* α -cyano- β -phenyl- γ -acetylbutyrate (III), very pale yellow, b. 196° . *Et* ester, similarly obtained in 50% yield from $\text{NCCH}_2\text{CO}_2\text{Et}$, very viscous oil, b. 203° . Semicarbazone of II, m. $156-7^\circ$. Boiled in coned. MeOH soln.

with 1 equiv. NaOMe, II gives I. Saut. in MeOH with HCl and allowed to stand, II gives 60% *di-Me* β -phenyl- γ -acetyldihydromalonate, $\text{PhCH}(\text{CH}_3\text{Ac})\text{CH}(\text{CO}_2\text{Me})_2$, m. 64°, which is more readily obtained like I from $\text{PhCH}:\text{CHCOMe}$, $\text{CH}_3(\text{CO}_2\text{Me})_2$ and NaOMe.

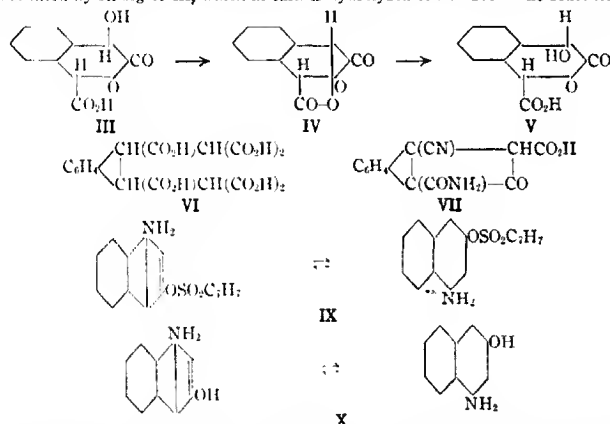
Syntheses in the indene series. IV. A. P. ORVEKHOV (WITH V. SHAPIR). *J. Russ. Phys. Chem. Soc.* 48, 1820-6 (1916); cf. *C. A.* 11, 3275. 2,3-Diphenylindene is synthesized by the dehydration with P_2O_5 of α,β,γ -triphenylpropene- α,β diol, m. 159-60°, prep'd. by the action of PhCH_2MgCl on benzoin. Dehydration with AcCl gives a 35% yield of the diphenylindene together with a 50% yield of monolactate of the diol, m. 176-7°, which is the sole product of the action of Ac_2O . V. A. P. ORVEKHOV. *Ibid.* 1827-9.—The method of the synthesis of indenenes from substituted bromopropenes by the elimination of HBr, is applied with success to the synthesis of indenones. COPh-CPHBrCHPhBr , is heated at 140-5°. A copious evolution of HBr takes place and an 89% yield of 2,3-diphenyl-1-indene is obtained.

The binary eutectics between naphthalene, iodoform, and iodine. A. M. VASIL'EV. *J. Russ. Phys. Chem. Soc.* 48, 1779-85 (1916).—The m. ps. and the compn. of the binary eutectic mixts. of C_{10}H_8 , CHI_3 , and I are det'd. in order to test the accuracy of a theory put forward by Flavitzkii (*J. Russ. Phys. Chem. Soc.* 37, 862-75 (1905)). According to this theory, where t_1 , t_2 , and t_3 are the m. ps. of 3 substances, of mol. wt. M_1 , M_2 , and M_3 , t_{1-2} , t_{2-3} , and t_{3-1} , the m. ps. of the eutectic mixts. obtained from each pair, and $n_{1-2}M_1 + M_2$, $n_{2-3}M_2 + M_3$, and $n_{3-1}M_3 + M_1$ are compns. of these eutectics, the following expressions are obtainable: $[n_{1-2}M_1(t_1 - t_{3-1})] / [M_2(t_2 - t_{3-1})] = \alpha$, $[n_{2-3}M_2(t_2 - t_{3-1})] / [M_3(t_3 - t_{3-1})] = \beta$, $[n_{3-1}M_3(t_3 - t_{3-1})] / [M_1(t_1 - t_{3-1})] = \gamma$. According to Flavitzkii, the product $\alpha\beta\gamma$ should be equal to unity. The results obtained for the systems $\text{C}_{10}\text{H}_8\text{-CHI}_3$, $\text{CHI}_3\text{-I}$, and $\text{I-C}_{10}\text{H}_8$ are in satisfactory agreement with this hypothesis, $\alpha\beta\gamma$ being 1.113.

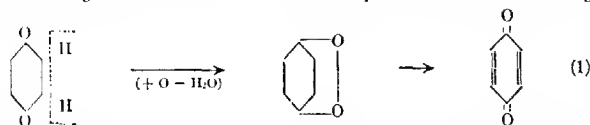
Hydroxynaphthoquinone studies. VI. Chlorination of juglone. A. S. WHEELER, P. R. DAWSON and J. L. MCLWEN. *J. Am. Chem. Soc.* 45, 1970-5 (1923); cf. *C. A.* 17, 104.—In CCl_4 there is little or no reaction between juglone (I) and Cl_2 but in hot AcOH dichlorojuglone (II), m. 149°, is smoothly formed. II in Et_2O shaken with 10% aq. Na_2CO_3 forms an indigo-blue Na salt, sol. in H_2O with deep violet color and regenerating II with acids; it dyes silk and wool buff and brown shades. 2,3-Dichloro-5-benzyoxy-1,4-naphthoquinone (0.64 g. from 0.5 g. II) boiled 3 hrs. in 5 cc. Et_2O , light yellow, m. 225°. 2,5-Dihydroxy-3-chloro-1,4-naphthoquinone (III), from II in boiling aq. alc. NaOH, red needles when wet, golden brown when dry, m. 191°, sol. in H_2O with deep red color instantly changed to yellow by acids and back to deep red on neutralization; 0.5 g. boiled 8 hrs. in Ac_2O gives 0.62 g. of the diacetate, yellow, m. 147°. 2-Nitroso-3-chloro-5-hydroxy-1,4-naphthoquinone (1.12 g. from 1 g. II and 0.4 g. PhNH_2 boiled 15 min. in alc.), violet-carmine with metallic luster, m. 222°. 2-p-Chloroanilino analog (0.8 g. from 1 g. II and 0.53 g. *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$), dark reddish purple, m. 213°. 2-p-Toluidino comp'd. (0.8 g. from 1 g. II and 0.44 g. *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$), dark reddish purple, m. 231°. 1,4,5-Trihydroxy-2,3-dichloronaphthalene (2 g. from 2 g. II in Et_2O suspension with 1:5 H_2SO_4 and Zn dust), gray with metallic luster, m. 157° (decompn.), gives with boiling Ac_2O the triacetate, light yellow, m. 182°. With NaOEt in C_6H_6 II gives III. NH_4OH does not react with II.

Structure of the benzene nucleus. III. Synthesis of a naphthalene derivative involving a bridged phase of the nucleus. The constitution of naphthalene and anthracene. W. A. P. CHALLENGER and C. K. INGOLD. *J. Chem. Soc.* 123, 2065-81 (1923); cf. *C. A.* 16, 2851.—In the theoretical portion it is pointed out that there is both chem. and crystallographic evidence that C_{10}H_8 (and the outer rings of $\text{C}_{14}\text{H}_{10}$, also) differ in some fundamental respect from the C_6H_6 ring itself and for this reason it seems desirable that all exptl. work carried out on the constitution of the C_{10}H_8 nucleus should as far as possible be paralleled in the $\text{C}_{14}\text{H}_{10}$ series. Expts. are described, the object of which is to produce by synthesis a bridged modification of the C_{10}H_8 nucleus in a manner similar to that in which the synthesis of the bridged phase of orcinol was accomplished. The starting point was *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{CO}_2\text{H})_2$. Treated with PCl_5 and then with dry Br, and finally poured into abs. EtOH it gave *Et* α,α' -dibromo-*o*-phenylenediacetate (I), red oil, which decomp. on distn. even at 10 mm. Attempts to prep. a bridged-ring structure by the action of aq. or alc. KOH, $\text{C}_2\text{H}_5\text{N}$, $\text{C}_6\text{H}_5\text{N}$, or PhNEt_2 on the chloride, however, gave α,α' -dihydroxy-*o*-phenylenediactic acid (II), m. 205°, in 80% yield. Ag salt, Dianilide, m. 208-9°. Heated at 110° II loses H_2O giving the lactone (III), m. 211-2° III, heated with AcCl , apparently underwent further dehydration, giving a dilactone (IV), which very easily passed into a monolactone (V), m. 179-80° upon crystn. from H_2O .

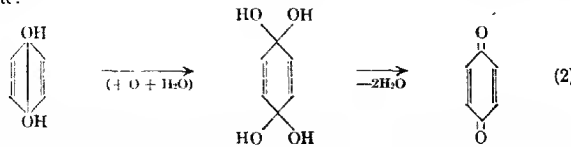
V is readily changed into III by keeping it in NaOH soln. for a few hrs. or by boiling with H₂O. The action of dil. NaOH upon the dibromo-chloride gave an 11-2% yield of II besides considerable amorphous acid. CHNa(CO₂Et)₂ and I in EtOH at a temp. below 10° gave [-CH(CO₂Et)₂]_n and an ester, which upon hydrolysis yielded the *hexacarboxylic acid* (VI), m. 187° (decompn.). Similarly the "monobromo-ester" gave a *pentacarboxylic acid*, m. 187° (decompn.). If *dibromo-o*-phenylenediacetonitrile, yellowish red oil which could not be distd., is treated at 0° for 10 days with CHNa(CO₂Et)₂ there results *4-cyano-1-carboxyamido-β-naphthol-3-carboxylic acid* (VII), cinnamon-colored, gives an olive-brown color with FeCl₃ and on distn. with soda-lime yields β-C₁₀H₇OH. Hydrolysis with HCl gives β-naphthol-4-carboxylamide, m. about 220° (decompn.). *p*-Toluenesulfonyl deriv. (VIII), pearl-grey, m. 210° (decompn.). The action of Br and KOH, followed by MeONa and NaOH, gave a mixt. of *4-amino-β-naphthol O*-*p*-toluenesulfonate (IX), pale yellow, m. 137°, and the free base (X), m. 198°. These products were also synthesized from 2,4-(O₂N)₂C₁₀H₆NH₂ through the diazo-oxide to 4-O₂NC₁₀H₆OH; *4-nitro-β-naphthyl p*-toluenesulfonate, pale yellow, m. 122°, is reduced by Al-Hg to IX, which in turn is hydrolyzed to X. IV. The reactivity of



bridged linkage. C. K. INGOLD. *Ibid* 2081-8.—One of the most noteworthy examples of the bridge linking is provided by the formation of quinones by oxidation of C₆H₆, PhOH, C₆H₄(OH)₂ and other derivs. of C₆H₆. Two possibilities are suggested: Direct removal of H to give Graebe's structure and the subsequent reversion of this to Fittig's:



The addn. of 2HO groups at the bridge and the subsequent dehydration of the quinone dihydrate:



To test this, di-HO-derivs. were carefully purified and the app. and chemicals thoroughly dried over P₂O₅ for 2 months, and control expts. made without special care as to the concn.

of H_2O . $\alpha\text{-C}_6\text{H}_4(\text{OH})_2$ with Ag_2O showed no difference in the rate of oxidation in the 2 cases, nor did $1,2\text{-C}_{10}\text{H}_8(\text{OH})_2$. $1,4\text{-C}_{10}\text{H}_8(\text{OH})_2$ showed no reaction during the 1st 6 hrs. heating with Pb_2O_4 although the reaction was complete in 10 hrs., while the control was complete in 2-3 hrs. The "period of induction" with $1,4\text{-C}_{10}\text{H}_8(\text{OH})_2$ was about 4 hrs. with the dry materials. This indicates the 2nd mechanism for the 1,4-derivs. and the 1st for the 1,2-derivs. These results are considered as preliminary and more crucial tests must be devised before the conclusions are positive. C. J. WEST

Aminonaphthols. J. MISSENDEN AND F. E. LECHE. *Chem. Trade J.* **73**, 35 6 (1923).—A review. T. S. CARSWELL

Anthracene series. V. E. DEB. BARNETT, J. W. COOK AND M. A. MATTHEWS. *J. Chem. Soc.* **123**, 1994-2008(1923); cf. C. A. **17**, 1636.—It is suggested that the first action of an oxidizing agent upon a phenol consists in the removal of the phenolic H atom, leaving a free radical in which the O atom is in the univalent state. These do not then combine to form a peroxide but rather stabilize themselves by changing over into free radicals with trivalent C atoms, the union of these with subsequent condensation leading to the diphenol. Evidence for this assumption is found in the C_{10}H_8 series, for anthrone and anthranol are distinct substances and dianthrone and dianthranol although interconvertible, are only so with difficulty. The present paper deals with the reestablishment of the "bridge" bond. Nitrodihydroanthranol is too unstable to be isolated and was studied as the As and Cl derivs. Hydrolysis with glacial AcOH and concd. H_2SO_4 gives dianthrone, while with cold $\text{C}_2\text{H}_5\text{N}$ $\text{C}_6\text{H}_5\text{N}_3\text{O}_2$ results. When hydrolyzed by AcOH-HI , $\text{C}_{10}\text{H}_{10}$ results. Thus the reestablishment of the "bridge" bond must take place by the loss of HNO_2 and the production of dianthrone is due to the direct oxidation of $\text{C}_{10}\text{H}_{10}$ by HNO_2 . The Cl deriv. behaved similarly. The Me ether in the presence of aq. NaOH or cold $\text{C}_2\text{H}_5\text{N}$ loses MeOH and gives a quant. yield of $\text{C}_{10}\text{H}_8\text{NO}_2$. The mechanism of the formation of the nitroanthrone may consist in the addn. of HNO_2 to the enolic anthranol and subsequent loss of H_2O ; to test this the nitration of anthranyl Me and Et ethers was studied. In neither case could any additive compd. be obtained; the reaction lead to a mixt. of nitroanthrone and dianthrone (approx. 2:1). In dibromodihydroanthracene the tendency to reestablish the "bridge" bond is very great, but in spite of this $\text{C}_2\text{H}_5\text{N}$ leads to a dipyrindinium salt. Bromoanthranyl Me ether does not react with $\text{C}_2\text{H}_5\text{N}$, but the combined action of HI and $\text{C}_2\text{H}_5\text{N}$ on anthranyl Me ether gives *methoxyanthranilpyridinium bromide*, decamps. about 195° ; analyzed as the *picrate*, golden yellow, m. $183-5^\circ$. NaOH gives a red ppt. at 80° . It is easily demethylated by HCl . *EtO deriv.*, analyzed as the *picrate*, golden yellow, m. $187-9^\circ$. Neither compd. is fluorescent. Anthrone, C_{10}H_8 and Br give hydroxyanthranilpyridinium bromide, m. $187-9^\circ$, previously obtained by treating bromoanthrone with $\text{C}_2\text{H}_5\text{N}$. Dianthranyl di-Me ether is conveniently prepd. by heating dianthrone with alc. KOH for 20 min. and then methylating with $p\text{-Me-C}_6\text{H}_4\text{SO}_3\text{Me}$. This ether is not demethylated by boiling HCl in AcOH . Anhyd. FeCl_3 in AcOH effects demethylation and at the same time oxidation to dianthraquinone. Nitro- and bromoanthrone pass very easily into dianthrone in the presence of such reducing agents as HI , H_2S in AcOH , $\text{AcCH}_3\text{NaCO}_2\text{Et}$ and MgPhI . PCl_5 reacts with anthrone to give $9,10\text{-C}_{10}\text{H}_8\text{Cl}_2$. In the presence of $\text{C}_2\text{H}_5\text{N}$ the product is a yellow powder, m. 303° , probably *trianthranil phosphate*. PCl_5 in $\text{C}_2\text{H}_5\text{N}$ does not attack anthrone. C. J. WEST

Reduction products of the hydroxyanthraquinones. H. JOHN HALL AND A. G. PERKIN. *J. Chem. Soc.* **123**, 2029-37(1923); cf. C. A. **16**, 1123.—Reduction of isanthraflavic acid anthranol in dil. NH_4OH with Al-Hg couple gives *2,7-dihydroxyanthracene*, darkens 250° , m. $280-5^\circ$ (decompn.); alc. and AcOH solns. display a violet fluorescence while H_2SO_4 gives a green fluorescent, reddish orange liquid, changing to deep bluish green on heating. Alc. FeCl_3 gives a greenish brown liquid, from which a dark colored ppt. soon seps. The disazo benzene deriv. is a crimson powder. The *di-Ac deriv.* m. 88° ; the *di-Me deriv.* m. $216-7^\circ$ and the *di-Et deriv.* m. $260-1^\circ$. *2,6-Dihydroxyanthracene*, darkens 270° , m. $295-300^\circ$ (decompn.), by the reduction of anthraflavic acid anthranol; the EtOH and AcOH solns. have a blue fluorescence, the pale yellow alk. solns. have a green fluorescence, rapidly disappearing in the air. H_2SO_4 gives an orange liquid, changing to a bluish violet on heating. *Di-Ac deriv.*, m. $260-1^\circ$. *Di-Me deriv.*, m. $255-6^\circ$. *Di-Et deriv.*, m. $230-1^\circ$. This is evidently Schuler's flavol (*Ber.* **15**, 1807). The bisbenzeneazo deriv. is maroon-colored and dissolves in concd. H_2SO_4 with a bluish green color. *1,2-Di-hydroxyanthracene* (cf. Lagodzinski, *Ann.* **342**, 104), m. $160-2^\circ$, results by the reduction of deoxylizarin; the orange alk. soln. quickly becomes blue and finally black on exposure to the air. *Di-Ac deriv.*, m. $157-7.5^\circ$. The Me and Et derivs. could not be obtained. In the same way 2-anthrol and anthra-

cene were prepd. A method of prepn. of isoanthraflavic acid from $C_{14}H_8O_2(SO_3Na)_2$ is given.

Pyranhydrones. IV. WILHELM SCHNEIDER. *Ann.* **432**, 297-318(1923); cf. C. A. **17**, 1013.—*4-Methyl-2,6-diphenylpyranhydron*, $C_{18}H_{16}O_2$, $C_{18}H_{14}O$, bluish red, sinters 55° , m. $90-105^\circ$, is best prepd. by adding 300 cc. satd. AcONa soln. to 1 g. methyl-2,6-diphenyl-pyrylium bromide in 100 cc. AcOH. If 2% HCl is used, a higher melting product is obtained, which probably contains some methylenepyrane, $C_{18}H_{16}O$. Heated at 125° , 1 mol. H_2O is split off, forming the pyran, a dark brown glassy compd. The pyranhydron is also decompd. by $HClO_4$. *2,6-Dimethyl-4-phenylpyrylium iodide* (I), m. 203° , results by the action of $PhMgBr$ upon dimethylpyrone in anisole, followed by KI in HCl. Upon quickly cooling an aq. soln. I seps. with a yellow color. On standing in contact with the mother liquor, it turns red. If the yellow crystals are quickly filtered off and dried the yellow color is permanent. *Periodide*, $C_{19}H_{18}O_4$, dark brown, m. $126-8^\circ$. In prepg. *2,6-dimethyl-4-phenylpyranhydron*, it is desirable to work at a low temp. (-10°) so that the compd. seps. slowly; it forms a chocolate-brown powder, sinters 60° , m. about 80° and decomp. at 140° (H_2O split off). *2,6-Dimethyl-4-phenylpyrylium iodide*, brown with violet metallic surface luster, m. 215° . Quickly cooled, the satd. EtOH soln. deposits a yellow modification. The *picrate*, yellow, m. 186° . The corresponding pyranhydron could not be obtained in a pure form. It forms a red-brown mass, the EtOH soln. of which has a Bordeaux-red color. Condensation of $PhCOMe$ or $dyponone$ with $(EtCO)_2O$ in the presence of H_2SO_4 , H_2O gives *2-ethyl-4,6-diphenylpyrylium sulfopropionate*, yellowish red, m. 163° ; with KI this yields the *iodide*, blood red needles, m. $230-7^\circ$. The action of AcONa or NaOH gives a red amorphous product, which is probably ethyldienepyrane, since it does not split off H_2O when heated *in vacuo*, does not change color when heated, and contains too little C for the pyranhydron. 2-Methyl-1,6-diphenylpyrylium chloride, heated with BzH_3 , gives the *2-styryl deriv.*, $C_{21}H_{18}OCl_2 \cdot 2H_2O$, red, m. 105° , (anhyd.), 115° . *Iodide*, dark brownish red needles, m. $183-4^\circ$. Treated with AcONa this yields an orange-yellow product, $C_{22}H_{18}O_2$, m. 120° , which is probably the pseudo-base.

C. J. WEST

The constitution of cantharidin. SAMUEL COFFEY. *Rec. trav. chim.* **42**, 387-436 (1923).—From a review of the previous work on cantharidin, especially after 1913, C. concludes that the formula accepted by Rudolf and later by Gadamer rests on insufficient exptl. evidence. In view of the extensive researches of Gadamer and his collaborators on cantharidin itself, it appears to be very difficult to institute further investigations of an analytical nature, which would lead to conclusive evidence that would definitely settle the constitution. C. therefore decided to prep. synthetically compds. having the 3 structures, originally suggested for deoxycantharidin by Gadamer, since by this means it should be possible to det. the constitution of the product from the natural source. Expts. were made to obtain *cis*-cyclohexane-1,2-diacetic acid (I) and its anhydride, since if G.'s 1st formula for cantharidin is correct these compds. should be identical with deoxycantharidic acid and deoxycantharidin, resp. Leroux (C. A. **5**, 681) obtained a product which he considers to be I but his method of prepn. from decahydro- β -naphthol is unsuited for its prepn. in quantity. Preliminary expts. proved that dibromocyclohexene reacted with $CHNa(CO_2Et)_2$ and this reaction was studied in detail but I was not obtained. The reaction takes place in 2 directions, giving cyclohexene and $[CH(CO_2Et)_2]_2$ (II) on the one hand and *Et tetrahydroisocoumaranone-2-carboxylate* (III) on the other. II reacts with N_2H_4 like a normal ester, giving *ethane-tetracarboxylic acid tetrahydrazide* (IV), m. 210° (decompu.). In order to confirm its constitution the *tetraacetonehydrazide* of IV, $C_{16}H_{20}O_8Na_2$, was prepd. by dissolving it in $COMe_2$ and evapg. the soln. spontaneously. It was thought that I could be prepd. from III, and the action of $CHNa(CO_2Et)_2$ (V) on halogenhydrins of cyclohexene was studied in order to obtain a good yield of III. The prepn. of cyclohexane 1,2-bromohydrin is described. The best method of prepg. III, which is the *lactone of cyclohexanol-2-carbethoxyacetic acid*, was from V and cyclohexene oxide. III could not be crystd. and b_p $190-200^\circ$ (decompu.). 2 g. crude III in an excess of EtOH-NH₃ for 2 days sepd. crystals of *cyclohexanol-2-malonamide*, m. $227-8^\circ$ (decompu.). 2 g. crude III in 20 cc. EtOH with 10 drops 90% $N_2H_4 \cdot H_2O$ sepd. *cyclohexanol-2-carbethoxyacetylhydrazide* (VI), m. $184-5^\circ$ (decompu.); the *acetone deriv.* m. $160-5^\circ$ (decompu.). On heating III or VI with excess $N_2H_4 \cdot H_2O$ *cyclohexanol-2-malonylhydrazide*, m. $226-7^\circ$, sepd. The constitution of the Na compds. produced by the action of V on cyclohexene oxide is discussed and expts. on the action of NH_3 , N_2H_4 and EtOH-KOH upon them are described. III treated with 10% KOH in EtOH gave the normal K *cyclohexanol-malonate* (VII), $C_8H_{10}(OH)CH_2(CO_2K)_2$. On acidifying the soln. of VII and extg.

with Et_2O α -carboxyhexahydroisocoumaranone was obtained as a viscous oil. **III** was obtained as a colorless liquid with a faint but characteristic odor, b_p 152.3°, b_m 138–9°, b_{78} 262.5–3.5°, $d_4^{12.5}$ 1.0925, $n_D^{12.5}$ 1.4790, m. p. –5.5°. **III** dissolves easily in warm alkalis. Solns. of *K* cyclohexanol-2-acetate (**VIII**) ppt. the lactone of **III** when acidified. **VIII** with AgNO_3 ppts. the 1g salt. **VIII** with dry HCl in cold abs. Et_2O pptd. KCl and on evapn. gave impure cyclohexanol-2-acetic acid, m. 97–102°. **III** with NH_3 - EtOH gave cyclohexanol-2-acetamide, m. 151°, stable toward heat and may be distd. without change. With $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ **III** gave cyclohexanodiacethydrazide, m. 167.5°; this boiled with BzH in EtOH gave cyclohexanol acetobenzhydrazide, m. 173.4°. **III** with PhNHNH_2 gave cyclohexano lactophenylhydrazide, m. 165.5°. **I** could not be obtained from **III**. Various attempts were made to find a better method for prepg. *o*-phenylenediacetic acid (**IX**) but that of Moore and Thorpe was found to be best. In this connection dihydronaphthalene was ozonized. The dihydronaphthalene monoosonide obtained was very stable and decompd. by H_2O only with great difficulty and failed in every case to give **IX**. **IX** is not acted upon by $\text{Na} + \text{EtOH}$ or AmOH , but is quantitatively reduced to a mixt. of *cis*- and *trans*-cyclohexanediactic acids with Pt black + H_2 . The sepn. of these 2 acids was very difficult but the *cis*-acid was obtained pure and it was definitely proved not to be identical with deoxycantharidinic acid. It may therefore be concluded that cantharidin is not a deriv. of this acid as has been suggested. Von Korczynski claimed to have prepared 4,5-dimethylphthalic acid from durene. His work was repeated and found to be incorrect. Durene on bromination at 130° in sunlight gives a complex mixt. of products from which it is possible to isolate a 10% yield of 2,4-dibromomethyl-1,5-dimethylbenzene, which was supposed to be the 4,5-dibromomethyl compd. of *v. K.* This compd. on hydrolysis and oxidation gives the corresponding dimethylisophthalic acid and not the *o*-phthalic acid as was supposed. Isophthalic acids with side chains *o*- to the CO_2H groups heated with resorcinol and H_2SO_4 give the fluorescein test owing to the oxidation of these side chains to CO_2H groups. When ZnCl_2 is used as the condensing agent these acids do not give the fluorescein test. Attempts to prep. 4,5-dimethylphthalic acid from 4,5-dibromo-*o*-xylene or 4,5-dibromophthalic acid failed. The action of $(\text{COCl})_2$ on *o*-xylene in the presence of AlCl_3 takes place in 2 directions giving *p*-xylyl chloride and 4,4'-*o*-xylyl, of which some derivs. are described. δ -Xylic acid is easily mercurated by heating with $\text{Hg}(\text{OAc})_2$ or by heating Hg *p*-xylate, giving a mixt. of the anhydrides of the 2 possible *o*-hydroxymercuri-*p*-xylic acids. The mixed hydroxymercuri compds. are easily converted into the corresponding *o*-sulfo-*p*-xylic acids, which are obtained pure by the fractional crystn. of the Ba and Na salts. These sulfo-*p*-xylic acids were orientated by treatment with aq. Br_2 in each case CO_2 and the SO_3H groups were eliminated with the production of known dibromo-*o*-xylenes. 4,5-Dimethylphthalic acid was prepd. by fusing the Na salt of 5-sulfo-*p*-xylic acid with HCO_2Na .

E. J. WITZUMANN

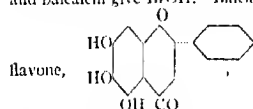
Catalytic reduction of nitro compounds. II. γ -Nitro ketones. E. P. KONTLER, *J. Am. Chem. Soc.* **45**, 2144–50 (1923).—Since γ - NO_2 ketones on hydrogenation should form substances in which active H and a $\text{C}=\text{O}$ group are in a relation favorable for intramol. condensation it was hoped that they might serve better than simpler nitro-paraffins to give an insight into the 1st step in the reduction of NO_2 compds. (the transition to NO compds. or oximes). The results with the 3 compds. studied, however, were disappointing, for while the reduction products undergo internal condensation, as expected, the condensation products are themselves so easily reduced that it is impossible either to confine the action to a single step or to deduce the successive steps from the final products. The results, moreover, depend to such a degree upon factors that cannot be controlled that both the nature of the products and their relative amts. vary in reductions which are carried out under as nearly as possible identical conditions. The reductions were carried out by shaking suspensions or solns. of the ketone in MeOH with H and Loew's Pt black. γ -Nitro- β -phenylpentanone, obtained in 48% yield from MeNO_2 and Na in MeOH with $\text{PhCH}:\text{CHCOPh}$, m. 99–100°; 40 g. on reduction until the absorption of H ceased yielded 27 g. 2-methyl- γ -phenylpyrrolidine, (I), b_p 112°, extremely hygroscopic, stable in sealed tubes but turns yellow in the air; reduction in Et_2O with BzCl and 10% KOH a 1-Bz deriv., m. 82–3°. 1,2-Dimethyl-4-phenylpyrrolidine-HBr, from I suspended in 10% KOH , treated with Me_2SO_4 extd. with Et_2O , dried and pptd. with dry HBr, m. 144–6° (probably with decompn.). β -3,4-Methylenedioxyphenyl- γ -nitrobutyrophene (II) (61 g. from 68 g. $\text{CH}_3\text{O}_2\text{C}_6\text{H}_4\text{CH}:\text{CHCOPh}$ and 30 g. MeNO_2), m. 95–6°; on reduction it absorbs H at a rate which remains practically const. until somewhat more than the amt. calcd. for reduction to the amine has been absorbed; the rate then drops sharply to nearly $1/4$ of its original value and remains at this level until absorption ceases. During the reduction the

γ -NH₂ compd. (III), m. 129–30°, seps.; it is stable when perfectly pure and dry but in soln. and when moist changes more or less rapidly into gummy discolored products; with PhSO₂Cl and alkali it gives 2-phenyl-1-[3,4-methylenedioxyphenyl]pyrrolone Ph *r*-sulfone, begins to turn brown 220°, m. 225–7° (decompn.). In a reduction carried out as nearly as possible in the same way as the preceding but interrupted when 31.3 g. II had absorbed only 4.97 l. II were obtained 7 g. unchanged II, 3.3 g. of a mixt. of II and III, 4.5 g. 1-hydroxy-2-phenyl-1-[3,4-methylenedioxyphenyl]pyrrolone, m. 144–5°, stable in air, does not reduce KMnO₄ in Me₂CO, and a gummy residue which on cautious treatment with HCl in MeOH + Et₂O yielded 2-phenyl-1-[3,4-methylenedioxyphenyl]pyrrolidine-HCl, m. about 208° (decompn.). O₂NCH₂CHPhCH₂CO₂Ph (IV) on reduction yielded only products which could not be distd. *in vacuo*. This oil with BzCl and KOH yielded 1- or 2-benzyloxy-2,4-diphenylpyrrolone, m. 179–80°; in MeOH-Et₂O the oil with HCl gave 2,4-diphenylpyrrolidine-HCl, m. 171–2°. Reduced in the presence of (CO₂H)₂, IV yields *d*-[2,4-diphenylpyrrolidine] oxalate. C. A. R.

The preparation of pure dehydrothiotoluidine. R. F. HUNTER. *J. Soc. Chem. Ind.* 42, 302T (1923).—100 g. *p*-MeC₆H₄NH₂ and 50 g. powd. S were heated 4–6 hrs. at 220°, after which the melt was cooled, powdered, and extd. with 30% H₂SO₄. NaOH sufficient to neutralize 0.5 the acid was added and the ppt. was filtered, washed, dried, and recrystd. from EtOH, when pale yellow crystals, m. 185° were obtained.

T. S. CARSWELL.

Baicalin, a new flavone-glucuronic acid compound from the roots of *Scutellaria baicalensis*. KEITA SHIBATA, SHOJIRO IWATA AND MAKOTO NAKAMURA. *Acta Phytochim.* 1, 105–39 (1923). The name scutellarin was applied by Takahashi to a cryst. compd. from *Scutellaria baicalensis*, to which he ascribed the formula C₂₁H₁₂O₈ (*Arch. pharmakol. Inst.* 239–43; *Chem. Zentr.* 1889, II, 100). The same name has, however, been accepted for a flavone-glucuronic acid compd. found by Molisch and Goldschmidt (*Monatsh.* 22, 679–99 (1901)) in other species of *Scutellaria*, and it is proposed to call T.'s compd. *wogonin* (from "wogon," the Japanese term for the root). A new compd., *baicalin*, closely allied to scutellarin, occurs in the roots of *S. baicalensis*, and can be extd. from the roots by boiling 50% alc., the yield being 12.5% of the weight of dry root. It is bright yellow, C₂₁H₁₂O₁₁, m. 223°. When hydrolyzed with concd. H₂SO₄, it is decompd. into glucuronic acid and a flavone deriv., *baicalein*, C₁₅H₁₀O₅, yellow, m. 264–5° (decompn.). A great deal of evidence indicates that baicalin is a tri-hydroxyflavone, a hydroxycyclysin with all 3 hydroxy groups in the one phenyl ring. By alk. hydrolysis, baicalin gives PhCOMe, and when fused with KOH both baicalin and baicalein give BaOH. Baicalein appears to be identical with the 5,6,7-trihydroxy-



prepd. synthetically by Bargellini, C. A. 14, 1527. Evi-

dence that condensation with glucuronic acid to form baicalin takes place at the 6-HO group is furnished by the observation that baicalin is not oxidized by chloropentamminecobaltchloride, which gives a strong color reaction with *o*-di-HO compds. but not with corresponding *m*-compds. Scutellarin likewise fails to give a reaction with this reagent, and must therefore be constituted similarly to baicalin. *Pentabenzoilscutellarin*, m. 237–8° (decompn.). Baicalin gives with FeCl₃ in alc. a dark green color, and with Pb(OAc)₂ an orange-red ppt. It dissolves in alkalies with a yellow color, and reduces NH₂AgNO₃ in the cold. It is difficult to alkylate, but forms with CH₂N₂ in acetone a *mono-Me deriv.*, m. 211–12° (decompn.); this contains a free CO₂H group. *Dibromobaicalin* softens above 270°. Baicalin is *D*-rotatory, $[\alpha]_D^{20} -144.9^\circ$. *Tetracetylbaicalin*, prisms contg. 1H₂O, m. 256–7°. The fact that only a tetra-Ac deriv. is formed indicates that the glucuronic acid is in the lactone form. A small quantity of what appeared to be a *pentaacetylbaicalin*, m. 212–13° (decompn.), was also obtained. *Tetra-benzoilbaicalin*, gray, m. 229–30°. *Tribenzoilbaicalin*, m. 199.5°. Triacetylbaicalin agrees in properties with Bargellini's tri-Ac deriv. of 5,6,7-trihydroxyflavone (*loc. cit.*). Free baicalein is present with baicalin in the roots of the plant. Further investigation of wogonin shows that the substance as analyzed by T. contained water of crystn. The correct formula is C₁₅H₁₂O₅, and it contains a MeO group. *Acetylwogonin*, C₁₇H₁₄O₆, m. 152–3°; *benzoylwogonin*, yellowish white, m. 170°; methylwogonin, C₁₆H₁₄O₅OMe, H₂O, yellowish white, m. 180–1°. Baicolein and scutellarein, like other hydroxyflavones (cf. C. A. 17, 3451) show two absorption bands in the ultra-violet, the bands showing shifts such as would be expected from the constitutions of the compds. In baicalin,

the first band disappears, only a broad band at 3500 remaining, but in scutellarin both bands persist, perhaps through the influence of the 4'-HO group. Wogonin has an unusual spectrum with only one band, at 3500, but acetylwogonin, like triacetylbaicalin, shows the true flavone spectrum. The green parts of *S. baicalensis* contain scutellarin. The relation between the scutellarin of the leaves and the baicalin of the roots is a question of great biochem. interest.

J. C. S.

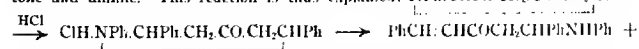
The action of sodium amide on pyridine as well as some observations on α -aminopyridine and some of its derivatives. J. P. WIDART AND ELISABETH DINGEMANSE. *Rec. trav. chim.* **42**, 240-50 (1923); cf. *C. A.* **17**, 2581. α -Aminopyridine (I) was synthesized by the method of Chichibabin and Zeide (*C. A.* **9**, 1901). W. and D. found that the course of the reaction depends greatly on the quality of the NaNH_2 used. Details on the prepn. of NaNH_2 and I are given. In working up the reaction products W. and D. obtained results differing from those of C. The product was distd. *in vacuo* in 2 fractions: (1) b_p 104-105°, was nearly pure I; (2) b_p 130-200°, was a colorless oil that darkened in the air. A dark brown thick mass remained in the flask. 55-65 g. I, b. 204-6°, were obtained from 100 g. $\text{C}_5\text{H}_5\text{N}$. I crystd. from C_6H_6 , m. 58.1-1°. 15-20 g. fraction (2) were obtained from 100 g. $\text{C}_5\text{H}_5\text{N}$ and sepd. 3.1 g. γ,γ -dipyridyl (II), m. 73°, which lost H_2O on crystn. in the desiccator and then m. 112°. In glacial AcOH II with Zn dust gives a violet color (Dimroth, Heine, *C. A.* **16**, 1591). II in EtOH with 2 mols. picric acid gave the *monopicate* of II. A portion of fraction (2) was dissolved in 25% HCl and sepd. first α,α' -dipyridylamine-HCl (III), m. 111-5°, and then the HCl salt of II. III treated with KOH soln. pptd. α,α' -dipyridylamine (IV), m. 95.2-5.4°; *picate* of IV, m. 227-8° (cf. Stenhausser, Diepolder, *C. A.* **11**, 3261). The mother liquor from III and the HCl salt of II was alkalinized with KOH and the brown oily liquid was subjected to further seps. A *base*, m. 73.5°, was sepd. The results in general show that by the action of NaNH_2 on $\text{C}_5\text{H}_5\text{N}$ in addn. to I, various by-products are formed and especially II and IV in considerable amts.; the formation of by-products was also observed by T. but other products were obtained. Schering (*Ger. pat.* 358397, *Chem. Zentr.* **IV**, 950 (1922), like W. and D., however obtained I, II and IV by the action of dry NH_3 with $\text{C}_5\text{H}_5\text{N}$ and Na in PhMe . The reason for the difference in behavior of different NaNH_2 preps. was not detd. It seemed possible that the formation of II was due to the free Na in the NaNH_2 prepn. but control expts. did not serve to establish the idea. W. and D. obtained a mono-Bz deriv., m. 87°, and a di-Bz deriv., m. 167°, of I which C. had described in the meantime (*C. A.* **16**, 3662). Acetyl α -aminopyridine and α -aminopyridylurethan (Camps, *Arch. Pharm.* **240**, 317) were prepd. and a crystallographic description is given. I treated with acid KMnO_4 is quickly oxidized. 0.1 to 0.3% aq. solns. of I treated with dil. KMnO_4 alk. with Na_2CO_3 is slowly oxidized. KMnO_4 with NaOH gives a characteristic green color reaction with I, which may be used to detect small amts. of it. I is fairly stable toward $\text{K}_2\text{Cr}_2\text{O}_7$ in neutral and alk. soln. I is slowly oxidized by acid $\text{K}_2\text{Cr}_2\text{O}_7$ soln. No definite compds. were obtained from these oxidations.

E. J. WITZEMANN

Alleged reaction of γ,γ -dipyridyl with potassium ferrocyanide. J. P. WIDART AND ELISABETH DINGEMANSE. *Rec. trav. chim.* **42**, 181-5 (1923). The formation of a blue color by the action of $\text{K}_4\text{Fe}(\text{CN})_6$ on γ,γ -dipyridyl HCl is not a sp. reaction for this case and may be struck out of the literature. The same holds true of the γ,γ -dimethyldipyridyl salt.

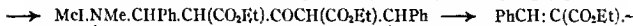
E. J. WITZEMANN

A reaction involving the rupture of the ring in heterocyclic compounds. I. P. PETRENKO-KRITCHENKO, E. PUTYATUI AND A. GANDELMAN. *J. Russ. Phys. Chem. Soc.* **48**, 1852-61 (1916).—The action of HCl and of MeI on some substituted 4 piperidones is investigated. HCl is passed through a benzene soln. of 1,2,6-triphenyl-1-piperidone. The HCl salt thus pptd. is treated with alkali, which liberates distyryl ketone and aniline. This reaction is thus explained:



$\text{HCl} \longrightarrow \text{PhCH} : \text{CHCOCH} : \text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_5 \cdot \text{HCl} \longrightarrow \text{C}_6\text{H}_5 : \text{CHCOCH} : \text{C}_6\text{H}_5 + \text{NH}_2\text{Ph} + \text{HCl}$. The ease with which the ring is broken in this compd. is due to the close proximity of the 3 Ph groups, as the corresponding *N*-Me compd. when treated in the same way regenerates the same compd. It appears also that the tri-Ph deriv. can be stabilized by converting the grouping $-\text{CH}_2\text{COCH}_2-$ into $-\text{CHR} \cdot \text{CO} \cdot \text{CHR}-$, where R is a CO_2Et group. The action of MeI on Et 2,6-diphenyl-1-methyl-4-piperidone-3,5-dicarboxylate is next examd. The III salt is prepd. by the action of MeI on the corresponding ester of diphenylpiperidonedicarboxylic acid, and the free I-Me ester, m. 85°, is obtained from it by the action of weak NH_3 . Prolonged boiling of

this substance with MeI merely results in the formation of its HI salt. The formation of this salt is explained as follows: $\text{NMe.CHPh.CH(CO}_2\text{Et).CO.CH(CO}_2\text{Et).CHPh}$



$\text{COCH(CO}_2\text{Et).CHPh.NMe}_2 + \text{HI}$. The HI thus liberated combines with unacted on 1-Me ester to form its HI salt. No other product was isolated from the reaction mixt. HCl passed through a benzene soln. of this ester gives a variety of products, of which only one is identified as the stereoisomeride, m. 138°, of the original substance, m. 85°. The action of MeI on *N*-methyltriacetouamine is to cause rupture of the ring. The latter substance is preparable by the action of MeI on triacetouamine, thus showing that the view held up to the present, that the homologs of the latter substance cannot be prepd. by direct alkylation, is incorrect.

J. C. S.

Preparation of crystalline alkaloid iodomercurates. MAURICE FRANÇOIS AND L. G. BLANC. *Compt. rend.* 175, 169-71; *Bull. soc. chim.* 31, 1208-16, 1304-14 (1922).—F. and B. prepd. cryst. alkaloid iodomercurates by heating a soln. of the alkaloid or its salt, contg. an excess of HCl, on a water bath, and adding it to a soln. of K iodomercurate. A small amt. of Na_2SO_3 was then added to prevent the liberation of I, and the mixt. cooled very slowly, giving the cryst. alkaloid iodomercurate. The products thus obtained were anhyd., contained no Cl, varied in color from yellow to orange, and in most cases were easily decompd. by H_2O . The quinine iodomercurate was, however, quite stable. The iodomercurates may also be crystd. from alc., this method being used for the cocaine compd., because cocaine is decompd. by HCl. For the analysis of the iodomercurates, they were heated with Na_2S , giving NaI and HgS . On filtering the I was detd. in the filtrate by pptn. with AgNO_3 . The HgS was converted to HgI_2 and the Hg detd. with Zn. The alkaloid was detd. in the iodomercurate by heating with Na_2S , acidifying, filtering, then making alk. with NH_4OH and extg. with CHCl_3 . The CHCl_3 was evapd. and the residue weighed as the alkaloid. This method could not be used for the morphine iodomercurate. The following cryst. alkaloid iodomercurates were prepd. and analyzed: *caffeine*, $\text{HgI}_2 \cdot \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{HI}$; *theobromine*, $\text{HgI}_2 \cdot \text{C}_7\text{H}_8\text{N}_2\text{O}_2\text{HI}$; *pilocarpine*, $(\text{HgI}_2)_2(\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\text{HI})_2$; *sparteine*, $\text{HgI}_2 \cdot \text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2\text{HI}$; *cocaine*, $(\text{HgI}_2)_2 \cdot \text{C}_{17}\text{H}_{21}\text{NO}_2\text{HI}$; *quinine*, $\text{HgI}_2 \cdot \text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{HI}$; *cinchonine*, $\text{HgI}_2 \cdot \text{C}_{21}\text{H}_{27}\text{N}_4\text{O}_2\text{HI}$; *strychnine*, $\text{HgI}_2 \cdot \text{C}_{27}\text{H}_{37}\text{N}_8\text{O}_2\text{HI}$; *codeine*, $\text{HgI}_2 \cdot (\text{C}_{18}\text{H}_{21}\text{NO}_2\text{HI})_2$; *morphine*, $\text{HgI}_2 \cdot \text{C}_{17}\text{H}_{19}\text{NO}_2\text{HI}$; *quinidine*, $\text{HgI}_2 \cdot \text{C}_{21}\text{H}_{27}\text{N}_4\text{O}_2\text{HI}$.

A. C. PURDY

Preparation of crystalline alkaloid iodobismuthates. MAURICE FRANÇOIS AND L. G. BLANC. *Bull. soc. chim.* 33, 640-54 (1923); cf. *C. A.* 16, 3663; 17, 1968.—For the analysis of the iodobismuthates, they were treated with a soln. of Na tartrate containing an excess of NaOH. The Bi and I passed into soln. and the alkaloid was liberated. The Bi was converted into the sulfide, then into the nitrate, and finally ignited and weighed as Bi_2O_3 . The I was obtained by pptn. with AgNO_3 and the alkaloid was extd. with CHCl_3 . The CHCl_3 was evapd. off and the residue weighed as alkaloid. The following cryst. iodobismuthates were obtained and analyzed: *caffeine*, $(\text{BiI}_3)_4(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{HI})_4$; *theobromine*, $(\text{BiI}_3)_4(\text{C}_7\text{H}_8\text{N}_2\text{O}_2\text{HI})_4$; *nicotine*, $(\text{BiI}_3)_4 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{HI}$; *sparteine*, $(\text{BiI}_3)_4 \cdot \text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2\text{HI}$; *arecoline*, $(\text{BiI}_3)_4(\text{C}_9\text{H}_{12}\text{NO}_2\text{HI})_4$; *pilocarpine*, red modification, $(\text{BiI}_3)_4(\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\text{HI})_4$; orange-red modification, $(\text{BiI}_3)_4 \cdot (\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\text{HI})_4$; *atropine*, $(\text{BiI}_3)_4(\text{C}_{17}\text{H}_{23}\text{NO}_2\text{HI})_4$; *quinine*, $(\text{BiI}_3)_4 \cdot \text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{HI}$; *morphine*, $(\text{BiI}_3)_4(\text{C}_{17}\text{H}_{19}\text{NO}_2\text{HI})_4$; *codeine*, $(\text{BiI}_3)_4(\text{C}_{18}\text{H}_{21}\text{NO}_2\text{HI})_4$; *aniline*, $(\text{BiI}_3)_4 \cdot (\text{PbNH}_2\text{HI})_4$; *pyridine*, $(\text{BiI}_3)_4(\text{C}_5\text{H}_5\text{NHI})_4$; *quinidine*, $(\text{BiI}_3)_4(\text{C}_{21}\text{H}_{27}\text{N}_4\text{O}_2\text{HI})_4$.

A. C. PURDY

Codeine and its isomers. EDMUND SPEYER AND WILHELM KRAUSS. *Ann.* 432, 233-65 (1923).—Allospseudocodeine (I) has been obtained cryst. and m. 116-7°, $[\alpha]_D^{25} -235.4^\circ$. Lees (*Ber.* 40, 4888) has reported a compd., m. 147.5°, believed to be a double compd. of I and isocodeine (II). The behavior on reduction in dil. AcOH with Pd-H confirms this view. *Tetrahydroallospseudocodeine* (III), m. 137-8°, $[\alpha]_D^{25} -75^\circ$, results in 90% yield from the reduction of I in dil. AcOH with Pd-H. Reduction of pseudocodeine with EtONa or electrolytically, using a H_2SO_4 soln., Pb electrodes and 10 amp., gives *dihydrospseudocodeine* (IV), m. 128°, which with Pd-H yields a tetrahydro deriv. (V). The *methiodide* of IV decomps. 275°; heated 15 min. with concd. KOH and then treated with $(\text{NH}_4)_2\text{CO}_3$, it yielded the *des-base*, oily, which gave an oily MeI deriv.; this split off Me_2N with 50% KOH. *Di-Ac* deriv. of I, m. 115°. *Di-Ac* deriv. of V, m. 137-8°. *Acetyldihydroisocodeine*, m. 168°. *Methiodide*, m. 268-9°. *I methiodide*, m. 252°. 50% KOH, followed by $(\text{NH}_4)_2\text{CO}_3$, gave *des-N-methyltetrahydroallospseudocodeine*, oily, and analyzed as the HI salt, m. 236°. The MeI deriv. was also oily, and after splitting off Me_2N with 50% KOH, only a brownish black oil was obtained.

des-N-Methyltetrahydropseudocodeine, m. 162-3°, readily resulted from the MeI deriv. of tetrahydropseudocodeine. Its MeI deriv. was oily and the N-free deriv. was also oily. **V**, in NaOH, treated with Me_2SO_4 and then NaI, gave the *Me ether methiodide*, m. 247°. This, also, did not give well defined decompn. products. *Dihydroscocodeine methiodide*, m. 272°. *des-N-Methyl-dihydroscocodeine*, m. 151°. *Methiodide*, m. 269°. This yields a N-free compd., $\text{C}_{17}\text{H}_{15}\text{O}_3$ (VI), m. 75-6°, $[\alpha]_D^{25} -160.1^\circ$. *des-N-Methyl-dihydrocodeine methiodide* yields the N-free compd., $\text{C}_{17}\text{H}_{15}\text{O}_3$, m. 115°. **I** and PCl_5 in CHCl_3 yield *allopseudochlorocodide*, $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{Cl}$, m. 151-5°. Reduction of the amorphous HCl salt with Pd-H and subsequent treatment with Me_2SO_4 followed by NaI gave a product identical with α -desoxytetrahydrocodeine Me ether methiodide, m. 249°. Attempts to chlorinate **II** with SOCl_2 failed. **V** and PCl_5 give *tetrahydropseudochlorocodide*, m. 103°. Reduction with EtONa gave a base, the HCl salt of which is identical with that of α -desoxytetrahydrocodeine. *Allopseudocodeine-N-oxide*, $\text{C}_{18}\text{H}_{21}\text{NO}_4 \cdot \text{EtOH}$ (VII), m. 212° (decompn.), results by the oxidation of **I** with excess H_2O_2 . *Isocodeine N-oxide* (VIII), m. 219° (decompn.). Sulfonation of VII (4 g. with 20 cc. Ac_2O and 3 cc. 96% H_2SO_4) gave 2 sulfonic acids, the less sol. in 280° (IX), the 2nd m. 271°. The sulfonic acids of VIII form leaflets, turning black at 300° or columnus decomp. 290°. The difficultly sol. form of *pseudocodeine-N-oxidesulfonic acid* decomps. above 300° and may be prepd. from the α form (X) by allowing the latter to stand with concd. H_2SO_4 for some time. An aq. suspension of IX, treated with Br and the perbromide decompd. by H_2SO_4 , gives *bromallopseudocodeine dibromide*, $\text{C}_{18}\text{H}_{19}\text{NO}_5\text{Br}_2$, m. 206-7°. The corresponding deriv. of pseudocodeine, m. 220°, of isocodeine, m. 212° and of codeine (XI), m. 200°. From X, a dibromide, m. 235° (decompn.), is obtained. Reduction of this bromide with Pd-H gives V, while reduction of XI gives dihydrocodeine. The action of Br upon dihydrocodeine-N-oxidesulfonic acid gives a mono-Br deriv., $\text{C}_{18}\text{H}_{21}\text{NO}_5\text{Br}$, analyzed as the methiodide, m. 230° (decompn.).

C. J. WEST

Taxine. II. E. WINTERSTEIN AND A. GUYER. *Z. physiol. Chem.* **128**, 175-229 (1923); cf. C. A. **16**, 3109.—The taxine content of yew leaves from different regions is quite uniform. Leaves from the male yews are richer. It is amorphous and the formula is now found to be $\text{C}_{27}\text{H}_{45}\text{O}_5\text{N}$. Iodomethyltaxine is $\text{C}_{27}\text{H}_{45}\text{O}_5\text{NCH}_2\text{I}$. 0.1 N alkali splits it into NMe_3 and $\text{C}_{26}\text{H}_{43}\text{O}_5$. Br treatment of the latter or of taxine with acids cinnamic acid results; oxidation with KMnO_4 gives BzH and BzOH . Treatment of taxine with 0.2 N alkali gives 1 mol. of AcOH , a little cinnamic acid and an amorphous nitrogenous compd. which still gives most of the taxine reactions. The last-named product and taxine itself with acids give a cryst. nitrogenous compd., $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$, m. 173-4°, which appears to be β -dimethylaminohydrocinnamic acid. The *chloroaurate*, m. 135-6°, the *chloroplatinate*, 208-10°. The tolerance of rabbits toward taxine may be increased three-fold. One mg. per kg. given intravenously raises the blood pressure slightly; 2 mg. is fatal. Hippuric acid is one of its decompn. products in the body.

R. L. STEHLER

Purification of essential oils, etc. (Brit. pat. 194,286) 17.

Fatty acid anhydrides. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GRS. Brit. 194,719, March 10, 1923. Anhydrides of fatty acids of low mol. wt. are produced by heating the fatty acids to a temp. above its b. p., the presence of catalysts which determine a decompn. of the acid in other directions being avoided. Thus, Ac_2O is obtained by rapidly conducting HOAc vapor over pieces of fireclay heated to 650°; propionic and butyric anhydrides are produced in like manner. The products are preferably quickly cooled; indifferent gases or vapors may be admixed with the acid vapor before it enters the heating zone; or liquids, such as volatile hydrocarbons, may be injected with the products of disoc. to assist the cooling and desirably to ppt. the H_2O formed. Catalysts may be present which favor the formation of the anhydrides, e. g., chlorides and sulfates of alkali and alk. earth metals, boric acid and borates.

Hydrazobenzene. F. B. DEHN. Brit. 193,663, Feb. 15, 1922. The reduction of nitrobenzene and its homologs to the corresponding hydrazo compds. by means of Zn and NaOH is effected, without application of heat, by adding at the beginning the full charge of Zn in the form of flakes, granules, or feathers, together with NaOH soln. or an equiv. thereof yielding with the Zn nascent H and sufficient heat to maintain the reaction temp. The reaction may be effected in any suitable heat-insulated vessel capable of being rotated or agitated. The hydrazo compds. may be converted into benzidine, etc., in known manner. A suitable app. is specified.

Esters. U. S. INDUSTRIAL ALCOHOL CO. Brit. 195,118, Nov. 11, 1921. An

app. for prepg. esters continuously by the process described in 195,117 consists of an esterification column, a combined preheater and dephlegmator therefor, a condenser connected to the latter, a rectifier for the condensate connected by a pipe to the esterifying column, a condenser for the rectifier, means for mixing the latter condensate with a regulated amt. of H_2O , a sepg. chamber for the mixt., and a second rectifier for rectifying the upper liquid layer. The production of $EtOAc$ from alc., vinegar and H_2SO_4 is described. Butyric acid, $MeOH$ and HCl are also mentioned as raw materials.

Hexamethylenetetramine. HOLZVERKOHLE-INDUSTRIE AKT.-GES. Brit. 195,602, March 1, 1923. CH_2Cl_2 is heated with aq. NH_3 at a temp. not materially exceeding 120° . An excess of NH_3 is desirable, while acid-binding substances, such as Na_2CO_3 or caustic alkalis, are preferably added to fix the liberated HCl . Examples are given in which (1) CH_2Cl_2 and aq. NH_3 are heated in an autoclave for 15 hr. at 100° , (2) CH_2Cl_2 , aq. NH_3 and $NaOH$ are heated at 105° to 110° in an autoclave for 20 hr.

Chlorine derivatives. DURAND ET HUGUENIN SOC. ANON. Brit. 193,843, Feb. 20, 1923. Highly chlorinated hydroaromatic products contg. N are prepd. by chlorinating hydrochlorides of aromatic amines with gaseous Cl in an indifferent liquid, moisture being excluded. Thus aniline- HCl , chlorinated first in cold and then in hot chlorobenzene, yields an octachlorochloroketiminohexahydrobenzene, and in benzene, if chlorination is stopped when dissolution has occurred chiefly a hexachlorochloroketiminoheptahydrobenzene. α - and β -Naphthylamines yield pentachlorochloroketimidotetrahydronaphthalenes; with β -naphthylamine the reaction is complete in cold benzene suspension but with α -naphthylamine a hot chlorobenzene suspension is necessary. α - and β -Aminoanthraquinones similarly yield pentachloro- α - or β -chloroketiminetetrahydroanthraquinone when chlorinated in benzene and chlorobenzene, resp. Examples are given of the prepn. of the above specified ketimines, the suspension of the amine hydrochlorides being first prepd. by passing gaseous HCl into benzene or chlorobenzene solns. of the parent amines.

Chlorination of methane. HOLZVERKOHLE-INDUSTRIE AKT.-GES. Brit. 195,345, Oct. 6, 1922. CH_4 is chlorinated by interaction with $SbCl_3$; the product comprises mainly CH_3Cl , but CH_2Cl_2 and $CHCl_3$ are also obtained. The reaction is preferably effected at temps. of 230 – 350° in the presence of distributing substances, such as refractory clay or pumice; but if a catalyst, such as the chloride of Cu, Fe or Ca, be present, the temp. of the reaction may be reduced to 250° . The $SbCl_3$ formed is preferably condensed and after re-chlorination is returned to the reaction chamber. Cf. C. A. 17, 289.

Chloroethyl compounds: amino compounds. BRITISH DYESTUFFS CORPORATION, LTD., W. H. PERKIN AND G. R. CLEMO. Brit. 193,618, Jan. 19, 1922. β -Chloroethyl *p*-toluenesulfonate (I) is obtained by heating $MeC_6H_4SO_3Cl$ with glycol chlorohydrin; it may be distd. *in vacuo*. In an example an excess of the glycol chlorohydrin is used. Ethylene ethers and chloroethyl ethers are obtained by interaction of I and alcs., phenol, cresols, *p*-nitro-*o*-cresol, naphthols, or aminophenols; in the latter case the amino groups are first protected; *o*- or *p*-nitrophenols do not readily give ethers by this process. The chloroethyl ethers obtained from the phenols, etc., react with arylamines or alkylamines such as $PhNH_2$, to give β -phenoxyethyl derivs. of the said bases; these derivs. yield nitroso compds. Examples are given. $(CH_3NH_2)_2$ derivs., chloroethylamines, and piperazine derivs. are prepd. by interaction of I and amines. Examples are given.

***p*-Aminophenol.** G. РОМА. Brit. 194,694, March 1, 1923. *p*-Phenol in alk. soln. is coupled with a diazo compd. from a primary aromatic amine such as benzidine, tolidine, α - or β -naphthylamine, or "an aminosulfonic, hydroxysulfonic, chlorosulfonic, carbonic, chlorocarbonic, or like base." The resulting azo compd. is reduced with H or "other reducing gas or mixt." in the presence of a catalyst; as catalysts are mentioned finely divided metals such as Ni, Co, Cu or Fe, and their oxides. The base is recovered by filtration, or in the case of benzidine or tolidine by addn. of Na_2SO_4 or H_2SO_4 and the *p*-aminophenol isolated from the remaining soln.

Cyanamide from calcium cyanamide. WARGOENS A.-B. and I. H. LIDHOLM. Swed. 53,529, Mar. 28, 1923. $CaCN_2$ and CO_2 are simultaneously introduced into water through sep. orifices while the liquid is kept in const. circulation.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A- GENERAL

FRANK P. UNDERHILL

Permeability of the cell: the surface as contrasted with the interior. R. CHAMBERS. *Proc. Soc. Exptl. Biol. Med.* 20, 72-4 (1922).—Starfish eggs stained with neutral red and immersed in a 5 M NH_4Cl soln. were penetrated by only the NH_4 group; when immersed in NaHCO_3 soln., only the CO_3 group penetrated. When these solns. were injected intracellularly with Chamber's microinjection apps., the effects of free HCl or NaOH were observed throughout the cells. The semipermeability of a living cell is a function of its surface film. C. V. B.

Can fasting fowls synthesize glycocoll or ornithine? J. G. M. BULLOWA AND C. P. SHERWIN. *Proc. Soc. Exptl. Biol. Med.* 20, 125-8 (1922).—Three chickens with artificial anuses were fasted 2 days and then given a total of 15 g. of BzOH in the succeeding 5 days; 63.3% of the unchanged BzOH and a small amt. of benzoylornithine were recovered from the urine. The test was repeated on 3 well fed hens and a total of 3.1 g. of benzoylornithine and 5.3% of uncombined BzOH were recovered, no hippuric acid was found. Birds are unable to produce or utilize glycocoll for purposes of detoxication. C. V. B.

Changes in the proteins and the gelatification of formalized blood serum. R. R. HENLEY. *J. Biol. Chem.* 57, 139-51 (1923).—The addn. of HCHO to serum causes a progressive decrease in the soly. of the proteins in $(\text{NH}_4)_2\text{SO}_4$ solns. The rate of transformation is proportional to the concn. of HCHO and may proceed to the complete disappearance of the albumin and pseudoglobulin fractions. With low concns. of HCHO , the transformation appears to reach an equl., independent of the concn. of the proteins, before it is complete. The rate of gelatification is proportional to the concn. of HCHO . With a given concn. of HCHO , the rate of gelatification is proportional to the concn. of the protein and the concn. of the salts. I. GREENWALD

Studies on autolysis. IX. Hydrogen-ion concentration in autolysis. E. L. SEVRINGHAUS, A. E. KOELER AND H. C. BRADLEY. *J. Biol. Chem.* 57, 163-79 (1923).—Following death, the H -ion concn. of liver cells (pH) increases very rapidly then more slowly to a pH of about 6 within 4 to 18 hrs. The acidity then falls to a pH of 6.6 in 10 days and then slowly increases again. If acid is added the initial high H -ion concn. sinks slightly for a few days until the bulk of the proteins are converted into amino acids. Thereafter, there is little change. The production of acid is the greater the amt. of alkali added and may change the pH from 9 to 7 in from 24 to 48 hrs. The greater part of the acidity produced is due to H_2PO_4 but fatty acids are also produced and the addition of the common fats makes the mixt. more acid and increases autolysis. The addn. of acids in equiv. amts. causes a proportionate increase in amino acids produced to a max. which appears to be reached when all available proteins have been converted into acid-protein salts. Further addn. of strong acids inhibits autolysis but an excess of acids such as HOAc does not increase the H -ion concn. sufficiently to destroy or inhibit the enzymes. I. GREENWALD

Postmortem acidity. I. The acids formed in autolyzing liver. E. L. SEVRINGHAUS. *J. Biol. Chem.* 57, 181-9 (1923).—The titratable acid content of sterile autolyzing pig liver increases with time but in simple mixts. of liver hash and H_2O and in those made alk., this increase is largely complete within 24 hrs. The amts. of acid produced in the simple and alk. mixts. are similar. In the alk. mixt., the relative importance of the acids is: H_2PO_4 , H_2CO_3 , fatty and lactic acids. The H_2PO_4 is at least 10 times as important as the lactic acid. In acidified mixts., the increase in amt. of acid goes on for a longer period and with the production of a larger amt. of acid, in which H_2PO_4 plays a less important part and in which some acid other than H_2PO_4 , H_2CO_3 , lactic or β -hydroxybutyric acid is formed. II. Phosphoric acid liberated in liver autolysis. *Ibid.* 57, 191-7 (1923).—Dog liver breis prepd. and kept at body temp. show a rapidly increasing content of inorg. P. The increase may be delayed by chilling in the prepn. of the brei. The liberation of inorg. P is increased by the addn. of alkalies and decreased by the addn. of acids. The liberation of inorg. P is believed to be, in part, a survival process. The lowest inorg. P contents recorded range from 12.6 to 19.7 mg. per 100 g. liver. I. GREENWALD

The relative precipitating capacity of certain salts when applied to blood serum or plasma and the influence of the cation in the precipitation of proteins. P. E. HOWE. *J. Biol. Chem.* 57, 241-54 (1923).—The mol. concns. of several salts required to ppt.

as much protein from serum or plasma as was pptd. by 0.75, 1.00, 1.25 and 1.50 *M* Na₂SO₄ at 37° was detd. and found to be: K₂SO₄, 0.75; Li₂SO₄, 1.00, 1.40, 1.80, 2.20; (NH₄)₂SO₄, 1.25, 1.50, 1.75, 2.00; MgSO₄, 1.25, 1.625, 2.00, 2.375; ZnSO₄, 1.25, 1.50, 1.75, 2.00; Na phosphate mixt., 0.90, 1.20, 1.50, 1.80; K phosphate mixt., 1.125, 1.425, 1.725, 2.025; NaCl, 3.75, 5.00; KCl, 3.75; LiCl, 5.00, 6.00, 7.00, 8.00. The absence of any one of the series of figures indicates that the salt in question was not sufficiently sol. to permit the detn. to be carried out. Attention is called to the regularity of increments of concn. needed for each succeeding fraction and to the fact that, although equiv. increments of base bear a simple numerical relation to each other, this is not a function of the valence. If the concn. of K remained the same, the ratio of KH₂PO₄:K₂HPO₄ could be varied from 1:16 to 8:1 without greatly changing the amt. of protein pptd. in the various fractions. The significance of the results is discussed. I. G.

The influence of the cation in the precipitation of the proteins of blood by sodium phosphate. P. E. HOWE. *Proc. Soc. Exptl. Biol. Med.* 20, 91-2(1922).—See above. C. V. B.

Oxidizing enzymes. VI. A note on tyrosinase. M. W. ONSLOW. *Biochem. J.* 17, 216-9(1923); cf. *C. A.* 15, 99, 2467.—All plants examd. which give the tyrosinase reaction also contain oxidase. Tyrosinase, it is suggested, is a mixt. of enzyme—a water-splitting enzyme (reductase or deaminase), a carboxylase and an oxidase (consisting of oxygenase, aromatic substance and peroxidase). BENJAMIN HARROW.

Adsorption and hemoglobin. A. V. HILL. *Nature* 111, 843-4(1923).—Answer to Bayliss (*C. A.* 17, 2292). One difficulty in the hypothesis that O and CO are "adsorbed" by hemoglobin lies in the highly sp. nature of the absorption spectrum of the compds. so formed. The change in color of reduced blood, or of a dil. soln. of reduced hemoglobin, when shaken with air or O, is obvious to the naked eye, as also is the change when the O is replaced by CO. These color changes can be used for the exact quant. measurements of the amt. of gas taken up. "Such remarkable, definite, and highly sp. changes in the absorption spectra have no parallel, so far as I am aware, in any well authenticated case of adsorption." J. BACROFT. *Ibid* 844.—According to Wo. Ostwald's adsorption theory (in reaction of O with hemoglobin), the graphic expression of the equation he suggests ($Y = K/C^n$, in which Y = amt. of O combined with hemoglobin, C = concn. of O in soln., K = quantity proportional to the total mass of hemoglobin present, and n = a const.) must necessarily be a simple curve which is at all points concave to the abscissa. "No published curve representing the equil. between hemoglobin and O, which has been detd. experimentally, is of this character, all being more or less S-shaped." N. K. ANAM. *Ibid* 844-5.—Hemoglobin in soln. is a heterogeneous system, possessing an interface which is very much too large to be satisfied by the amt. of O which is actually taken up at satn., and therefore the O must be held by some other means than adsorption. W. E. L. BROWN. *Ibid* 881-2.—Further argument in favor of view that combination of hemoglobin with O and CO is chem. B. H.

The effect of high and low temperatures on the catalase content of *Paramecium* and *Spirogyra*. W. E. BURGE. *Am. J. Physiol.* 65, 527-33(1923).—Low temps. decrease and temps. above normal increase the catalase content of *Paramecium* and *Spirogyra*. This is further evidence of the parallelism between catalase and rate of oxidation in tissues. J. F. LYMAN

Hemolytic action of radium emanation. A. C. REIDFIELD AND ELIZABETH M. BRIGHT. *Am. J. Physiol.* 65, 312-7(1923).—The destruction of red blood cells by Ra emanation is due chiefly to the action of α -rays. Hemochromolysis and stromatolysis proceed independently of each other. The elec. resistance of the suspension of erythrocytes increases as hemochromolysis proceeds, and is reduced again when stromatolysis occurs. J. F. LYMAN

The sensitization to heat due to exposure of short wave lengths. Influence of ozone. H. S. FORBES AND G. A. DALAND. *Am. J. Physiol.* 66, 50-4(1923).—*Paramecium caudatum* exposed to ultra-violet light in a fluorite chamber may be killed either by the direct action of the rays or by the O₃ formed. Heat following strong radiation has apparently a more lethal effect than preceding it. J. F. LYMAN

The sensitization of protoplasm to heat by exposure to light of short wave length. W. T. BOYD AND G. A. DALAND. *Am. J. Physiol.* 66, 55-66(1923).—Previous expts. (*C. A.* 13, 879) are open to criticism because of the spurious effects of the O₃ generated by the fluorite rays to which the organisms were exposed. The expts. have been repeated, under conditions which exclude the influence of O₃ and the earlier conclusion is confirmed, viz., sub-lethal exposure to fluorite rays renders the organism (*Paramecium caudatum*) extremely sensitive to heat, so that it is injured and killed by an amt. of heat which would not affect a normal unradiated individual. It is suggested that the

uniqueness of the biological effects of radiation lies in the fact that the rays form within the cell chem. combinations which are foreign to normal protoplasm. The radiated organism which has not been exposed to an increased temp. may appear quite as normal as if the rays had no effect whatever. It is only when the initial photo chem. change, "latent image," has been "developed" by the metabolic changes occurring at higher temps. that the effects of the exposure are to be observed.

J. F. LYMAN

Phase reversal in emulsions and protoplasm. WM. SCHULTZ. *Am. J. Physiol.* 66, 124-39 (1923); cf. *C. A.* 17, 2891.—The effects of various electrolytes (NaOH, NaCl, Ba(OH)₂, BaCl₂ and CaCl₂) in causing phase reversal in emulsions of (1) oil in water and (2) water in oil, prep'd. with various emulsifying agents, were studied. Olive oil emulsions with casein, gliadin, cholesterol, or cephalin in the aq. phase, form water in oil systems which are reversible with NaOH. Oil emulsions, in which saponin (seneggin, smilacin), gelatose, gum arabic, albumin, lecithin, or plant ext., is the emulsifier, form oil in water systems which are not reversible with BaCl₂. The hypothesis of Clowes (*C. A.* 10, 1753) on the mechanism of permeability changes in the plasma membrane of organisms is based on the behavior of only one type of emulsion in the presence of certain ions and must be regarded as a purely speculative hypothesis which rests on very uncertain evidence.

J. F. LYMAN

The adrenaline and vagal types of apnea. J. MELLANBY AND A. ST. G. HUGGETT. *J. Physiol.* 57, 395-404 (1923).—In animals (cats and rabbits) under urethan anesthesia the apnea caused by injecting 1 cc. of a 0.01% adrenaline soln. is prevented by the previous injection of ergotoxin intravenously. The apnea caused by stimulating the central end of the cut vagus is not affected by ergotoxin. It is believed that adrenaline causes constriction of the blood vessels of the respiratory center, thus depriving them of the normal stimulus of the H ions of the blood. In the case of vagal apnea the afferent nervous impulse so affects the membranes of the cells that they become impermeable to the H ions of the blood.

J. F. LYMAN

The fate of some halogen derivatives of benzene and of benzene in the animal body. T. S. HELE AND R. L. CALLOW. *Proc. Physiol. Soc., J. Physiol.* 57, xliii (1923).—C₆H₅Cl administered to dogs is excreted in part as chlorophenylmercapturic acid and in part as C₆H₄ClHSO₃. The increased S excretion following administration of halogen derivs. of C₆H₅ agrees very closely with that cited, on the basis of the above from the org. halogen of the urine. This would suggest that there is only one etheral sulfate and one mercapturic acid present, each contg. an aromatic nucleus, to which the halogen is still attached and that in no case is the halogen liberated before either synthesis takes place. The following compds. were tested: C₆H₅Cl, *o*-C₆H₄Cl₂, *m*-C₆H₄Cl₂, *p*-C₆H₄Cl₂, ClOCH₃ and C₆H₆.

J. F. LYMAN

The etheral sulfate and mercapturic acid synthesis in the dog. T. S. HELE. *Proc. Physiol. Soc., J. Physiol.* 57, xlii (1923).—The failure of Rhode (*C. A.* 17, 2328) to demonstrate the direct synthesis of PhOH with sulfate to form etheral sulfate in the body was due (1) to the mode of administration of the sulfate and (2) to the smallness of the doses of PhOH as compared with the daily output of sulfate from the rat-diolized protein. If small doses of PhOH are replaced by large doses of the non-toxic guaiaacol and the sulfate is given by mouth, direct evidence of their union may be obtained. In expts. from 60 to 80% of the administered sulfate was excreted as etheral sulfate. Similarly C₆H₅Cl after oxidation to C₆H₅ClOH will unite with sulfate to form etheral sulfate or with cystine to form mercapturic acid. When dogs were kept on a standard diet and C₆H₅Cl or C₆H₅Br was administered by mouth the increased urinary etheral S and mercapturic acid S showed a rather constant ratio of about 1 to 2. It is doubtful if this ratio can be upset by giving cystine by mouth because of oxidation of the cystine before the seat of synthesis is reached.

J. F. LYMAN

Aluminium hydroxide. I. Hydrates and hydrogels. RICHARD WULFSTÄTTER AND HEINRICH KRAUT. *Ber.* 56B, 149-62 (1923).—Different kinds of alumina were used to det. whether the cause of variation in the activity as an adsorbent of enzymes is the formation of chem. compds. (hydrates) and whether the adsorption activity and chem. properties are so related as to differentiate the kinds of alumina. Al(OH)₃, A, B, C and D was prep'd. as follows: (A) 500 g. Al₂(SO₄)₃ 18H₂O in 1½ l. H₂O was heated to b. p. and poured in a fine stream into 5 l. of 20% NH₄OH previously warmed to 50° and briskly stirred during the addn. While heated moderately a slow current of steam was passed through this mixt. for 5 hrs. After washing 4 times by decantation with 12-20 l. of H₂O, the ppt. was heated 48 hrs. under a reflux condenser to gentle boiling with 3 l. of 20% NH₄OH, and then washed by decantation till SO₄-free. During this heating a total of 1½ l. of 20% NH₄OH was added. B and C were prep'd. in the same way with these exceptions: (B) no steam was used. In the first pptn. and in the

later treatment of the ppt. with 4 l. of 20% NH_4OH , the mixt. was heated to 60–70° for only $\frac{1}{2}$ hr. C was pptd. in dil. NH_4OH ($1\frac{1}{2}$ l. 20% NH_4OH + 6 l. H_2O) and the time of heating both for the original pptn. and the later treatment with 4 l. of the dil. NH_4OH was $\frac{1}{4}$ hr. at 60–70°. (D) 130 g. $\text{Al}(\text{OH})_3$ was dissolved in KOH (140 g. + 900 cc. H_2O) dild. to 1 l., filtered, dild. to 10 l., pptd. by CO_2 and washed free of salts. A was a yellow, plastic mass; B, a light yellow, viscous, plastic mass; C, a pure white, voluminous, extremely fine powder; D, a pure white, coarse powder. In 1% NaOH , A, C, and D were insol. and B was slowly sol. In 12% AcOH , A and B were completely peptized and C and D were insol. In 1% HCl , A, C and D were insol. and B was easily peptized and showed strong Tyndall effect. In 35% HCl , A was difficultly sol., B slowly sol. and C and D were easily sol. When dried in a desiccator over H_2SO_4 and the $\frac{1}{2}$ H_2O detd. by heating to glow, A corresponded very closely to $\text{Al}_2\text{O}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$, B to $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, C to $\text{Al}_2\text{O}_3 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ and D to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. When dried at a series of 10° temp. intervals between 40° and 210° in a current of air previously satd. with H_2O (vapor) at 18°, evidence of hydrates at certain temps. was obtained for A and B. When invertase, prepd. from yeast (cf. C. A. 16, 3320; 17, 2294), was used, the adsorption value of the $\text{Al}(\text{OH})_3$ was increased many times by dild. The adsorption values (quantity of enzyme adsorbed by 1 g. of Al_2O_3) of the different kinds of alumina were in the order B or C > A > D. There seemed to be no simple relation between the colloidal properties and the adsorption activity of $\text{Al}(\text{OH})_3$ gels. Both the conditions which tend to increase the surface and the ability to react chemically seemed to influence the adsorption activity. The relation of these 2 factors varied with different enzymes, e. g., for lipase, dild. did not cause an increase of the adsorption value. The difference between B, A and D in ability to adsorb lipase or peroxidase was not so great as with invertase. While B and C adsorbed invertase equally well, the adsorption of lipase or peroxidase by C was much less than B.

H. M. McLAUGHLIN

The effect of various salts on tryptic and ereptic activity. KAZUO NAGAI. *J. Biochem.* (Japan) 2, 229–37(1923).—The trypsin and erepsin used in these expts. were obtained from dogs through special fistulas; the enterokinase was made by the usual method from the upper part of the intestine. As substrate a casein soln. prepd. by the Van Slyke method and elupeine sulfate by the Kossel method were employed. The optimum activity of trypsin was at $p_{\text{H}} = 8.2$. Trypsin is affected by electrolytes in a manner similar to that of pepsin, and its action is accelerated by multivalent anions. The optimum p_{H} for the ereptic activity is 8.0, and this activity is accelerated by both multivalent anions and cations. This last fact is taken to indicate that salts may influence the ereptic action by exerting its effect partly on the substrate and partly on the enzyme.

S. MORGULIS

Behavior of calcium phosphate and calcium carbonate (bone salts) precipitated in various media, with applications to bone formation. J. C. WATT. *Biol. Bull. Marine Biol. Lab.* 44, 280–308(1923).— $\text{Ca}_3(\text{PO}_4)_2$ pptd. in water or in colloidal solns. is constantly granular and amorphous in character, and apparently uninfluenced by the nature of the soln. CaCO_3 pptd. in H_2O shows a great diversity of cryst. form; in colloidal solns. it shows two main forms, one irregular cryst. and the other spherical. Mixts. by simultaneous pptn. of both salts in the same soln. show each salt segg. out independently and the part of the deposit formed by each can be easily identified. Spherules and crystals are influenced in shape, size, number and internal structure by a variety of substances found normally or pathologically in the blood, most notably by lecithin which favors the formation of large spherules, and by acetone which increases the rapidity and extent of the pptn. The character of the deposit of CaCO_3 is influenced by the H-ion concn. of the colloidal soln., being most cryst. in acid media, all in the form of spherules in strongly alk. media, and mixed in form in neutral or nearly neutral solns. Large spherules after persisting for months may undergo a sort of degenerative process, with change of internal structure, after which they dissolve and the material forming them is laid down in cryst. form, a phenomenon which probably has not been previously described. In fresh bone of various animals there is no microscopic evidence of the bone salts, although they form two-thirds of the matrix. The inference is that the bone salts are not deposited in the matrix by simple pptn. for the conditions are such that if pptd. granules, spherules and crystals should be visible. In the rapidly developing fetal skeleton the first appearance of bone in the matrix is in the form of fine granules or globules which quickly fuse to form a homogeneous mass. This might be interpreted according to the bias of the observer as supporting evidence either of pptn. or of secretion of the salts into the matrix. The view advanced by Barillé and supported by Wells' work, that Ca is carried by the blood as tribasic calcium carbonophosphate, is probably correct as it furnishes the bone salts in the proper proportions, but their

view of its deposit in the matrix as a ppt., due to change in the concn. of CO_2 , does not appear correct in view of the fact that no ppt. of the bone salts is visible. The theory that salts furnished by the blood are taken by the bone cells and secreted by them along with the matrix seems reasonable in view of the condition found in the matrix. The action of the osteoblasts appears to be reversible; they are able to take up again the Ca salts of the matrix.

L. W. REAGS

Intimate phenomena of respiration. JULES AMAR. *Compt. rend.* 177, 350 2 (1923); cf. *C. A.* 17, 2293.—The object is to show that the phenomenon of oxidation, which is the essence of the respiratory act in all life, is not a protoplasmic phenomenon or only in an accessory manner. The adsorption of O at the surface of the red cells of the blood is calcd. mathematically. The hematic absorption is subordinate to the previous soln. of the O in the blood. The true functions of the red cells are to increase the reserve O by the absorption of O, and to regulate this reserve O in the higher animals.

L. W. REAGS

Effect of amino acids in retarding the hydrolytic decomposition of an enzyme (pancreatic amylase). H. C. SHERMAN and FLORENCE WALKER. *J. Am. Chem. Soc.* 45, 1960-4 (1923); cf. *C. A.* 16, 571.—Positive evidence was given in the earlier papers that the favorable influence of NH_2 acids upon the action of amylases is due, at least in part, to the fact that they prevent or retard the deterioration of the amylase in its aq. soln. This has been studied in 3 ways: (1) the losses in activity of equal portions of the same enzyme soln. were compared after they had stood in the absence of substrate for a definite length of time at known temps., alanine having been added to some of these portions and not to others; (2) the effect of temp. upon "activation" was detd.; (3) a similar series of expts. was carried out in which the enzyme was allowed to act at these same temps. for a longer time. It was found that highly purified preps. of pancreatic amylase, which deteriorate more rapidly in aq. soln. than other preps. studied, are also more affected by NH_2 acids than the weaker preps. Solns. of amylase (contg. optimum concns. of chloride and phosphate) which have stood 1 hr. at 40° show considerably greater activity when alanine has previously been added. Solns. contg. no chloride and phosphate deteriorate more rapidly and the protective effect of the NH_2 acid can be demonstrated at lower temps. There is a striking increase in apparent activation by glycine and phenylalanine with increased temp. of digestion until coagulation of the enzyme occurs. At the same temps. there is greater apparent activation when hydrolysis is allowed to proceed 1 hr. than when it is stopped after 30 min.

C. A. R.

The influence of various preparations of the quinine group on the fermentative function of the organism. The influence of some quinine and urea compounds on the α -proteases. J. A. SMORODINTZEV and A. N. ADOVA. *Biochem. Z.* 135, 128-11 (1923).—The influence of quinine preps. on tryptic digestion of casein was studied by the Fuld-Gross method (a) by detg. the speed of reaction after adding various preps., and (b) by detg. the minimal amt. of quinine prep. necessary to produce the characteristic inhibition or acceleration. The following solns. retard digestion: 0.05-0.0016 *N* quinine-HCl, 0.0016-0.0002 *N* quinine- H_2SO_4 , 0.0062-0.0004 *N* urea-HCl, 0.0062-0.0008 *N* urea- HNO_3 , and urea- H_2SO_4 , 0.0032-0.0004 *N* quinine urea-HCl, 0.0031-0.0002 *N* quinine- H_2SO_4 . The following accelerate: 0.05-0.0125 *N* urea-HCl and urea- H_2SO_4 , 0.05-0.0062 urea- HNO_3 , 1.0-0.05 *N* quinine urea-HCl. The above preps. in greater diln. than above mentioned, and 0.05 *N* urea show no effect. In quinine-HCl and quinine- H_2SO_4 the retarding effect is detd. by quinine itself, as the effect is independent of the anion. The accelerating influence of quinine urea depends on the urea-HCl in the molecule. The influence of quinine urea is the algebraic sum of the influence of quinine-HCl and urea-HCl. Strong enzyme solns. require a higher concn. of quinine or urea compds. to exhibit the retarding effect. This shows that they act on the enzyme itself, and not on the substrate.

GEORGE ERIC SIMPSON

The reaction of yeast enzymes to high temperatures. S. AKAMATSU. *Biochem. Z.* 137, 364-71 (1923).—An acetone prep. of yeast showed zymase and carboxylase activity after heating to 120° in toluene for $\frac{1}{2}$ hr. Treatment with boiling xylene for 15 min. did not destroy the activity of either enzyme, though heating for $\frac{1}{2}$ hr. did. Carboxylase activity was affected by heat less than zymase activity.

G. E. S.

The action of emulsin on the system: hydrogen cyanide benzaldehyde mandelonitrile. F. NORDEFELDT. *Biochem. Z.* 137, 489-95 (1923); cf. *C. A.* 15, 2887; 17, 1249.—The rate of cleavage of *d,l*-PhCH(CN)OH is independent of the presence of emulsin; it is detd. by C_H . *d*-PhCH(CN)OH is more swiftly hydrolyzed than its optical isomer; thus an excess of the latter accumulates. In time this is racemized; racemization is more rapid the nearer the acid soln. approaches neutrality. Aeration of the

reaction mixt. hastens oxidation of the product C_6H_5CHO , with the result that the increased acidity diminishes the speed of racemization. GEORGE ERIC SIMPSON

Glycerophosphatases of plant seeds. ANTONIN NĚMEC. *Biochem. Z.* 137, 570-5 (1923); cf. *C. A.* 13, 2901.—The reaction follows Schütz's rule. It does not go to completion. The optimum is about 35°. Glycerol up to 1% favors the reaction by increasing the soly. of the enzyme. Greater concns. inhibit. Soy bean, and yellow and white mustard seed were the sources of the enzyme. GEORGE ERIC SIMPSON

Effect of Röntgen rays on proteins. I. P. WELS. *Arch. ges. Physiol* (Pflüger's) 199, 226-36 (1923).—Under certain circumstances, not entirely clear but probably associated with the englobulin content of the soln., the exposure of protein solns. to Röntgen rays results in coagulation phenomena. The viscosity of serum and of globulin solns. increases under treatment with the rays. With albumins the increase occurs only at the isoelec. point. Irradiation diminishes the surface tension of serum and of solns. of albumins and globulins, although this effect is modified greatly by the acidity or alkyl. of the solns. G. H. S.

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B—METHODS AND APPARATUS

STANLEY R. BENEDICT

The detection of blood for legal purposes by means of hemochromogen and its crystals. PUPPE. *Dent. Z. ges. gerichtl. Med.* 1, 663-7 (1922); *Chem. Zentr.* 1923, II, 125.—The method devised by P. (cf. *C. A.* 5, 305) has proved of value and the following procedure is now recommended. Particles of the substratum are scraped off and treated on a microscopic slide with freshly prepd. hydrazine-sulfate- C_2H_5N mixt. (3 parts satd. aq. hydrazine-sulfate, 2 parts C_2H_5N). Two cases in which the procedure failed, on account of changes in the compn. of the blood due to chemicals, are described. C. C. DAVIS

A new chemical method for the detection of bilirubin, with special application to the study of bilirubinemia. GIUSEPPE SABATINI. *Policlinico* 29, 837-42; *Ber. ges. Physiol.* 15, 92; *Chem. Zentr.* 1923, II, 78.—Add 1-1.5 cc. of serum to 0.3-0.4 cc. of a mixt. of 30 cc. 3% HCl + 0.5 cc. 0.5% $NaNO_2$. In the presence of bilirubin a bright green color appears immediately, becoming dark green, then blue green and eventually losing color, though still visible after 24 hrs. Cl ion appears to be necessary for the reaction. The limit of sensitiveness is 1:200,000. Normal serum gives a pale green color after long standing (physiological bilirubinemia). C. C. DAVIS

Refractometric and viscosimetric investigations of blood serum. FRITZ ROHRER. *Schweiz. med. Wochschr.* 52, 555-60 (1922); *Ber. ges. Physiol.* 15, 412; *Chem. Zentr.* 1923, II, 164; cf. *C. A.* 17, 1992.—A study of the influence of the non-albuminous components of blood on the results by the refractometric method of Reiss confirmed the values of Reiss when the fats and lipoids of the serum were taken into consideration. The increase in refraction for 1% of serum albumin was higher than that found by Reiss (178:172), whose tables are however but slightly changed. Investigation of pure albumin and globulin solns. gave further support to the validity of the principles of the method devised by R. for the detn. of the proportions of serum proteins by refraction and viscosity. Drying of the globulin or long time of prepn. leads to considerable increase in viscosity. C. C. DAVIS

The relation between the albumins and the globulins of serum (albumin quotient) and the Rohrer process. FRED WANNER. *Schweiz. med. Wochschr.* 52, 785-9 (1922); *Ber. ges. Physiol.* 15, 413; *Chem. Zentr.* 1923, II, 164.—A criticism of the methods of Rohrer (cf. preceding abstr.), based on observations during the reabsorption of an edema and the great differences in the albumin quotient on diln. of the serum with H_2O , HCl or Na_2CO_3 soln. C. C. DAVIS

The determination of the proportions of albumin-globulin mixtures in blood serum. Remarks on the investigation of Dr. F. Wanner. FRITZ ROHRER. *Schweiz. med. Wochschr.* 52, 789-90 (1922); *Ber. ges. Physiol.* 15, 413-4; *Chem. Zentr.* 1923, II, 164.—The criticism of Wanner (cf. preceding abstr.) is not accepted. The method has been perfected only for conditions where all but the concn. of the albumin remains unchanged. Clinically its use is excluded only with uremia and hyperglucemia. C. C. DAVIS

The determination of the real acidity and of the total acid in the stomach contents. H. VBS. *Nederland. Tijdschr. Geneeskunde* 66, 2, 22 (1922); *Physiol. Abstracts* 8, 103.—

Günzberg's reagent is recommended as indicator for free acid, and rosolic acid or neutral red for total acid.

A new method for accurately determining the clotting time of the blood. H. G. PETERSEN AND C. A. MILLS. *Arch. intern. Med.* 32, 188 (1923). Capillary tubes of 0.6–0.8 mm. inside diam. are cut into lengths of about 2.75 cm. The blood is drawn from a stab wound of the finger or ear. The first drop is wiped off, the tube is touched to the second drop and filled by capillarity until all but 0.5 cm. is filled. The tube is then placed in a crease of the palm, the hand closed over it, and slowly inverted every 30 seconds until the blood no longer moves along the tube. Time is counted from the appearance of the second drop above the wound. Detns. do not differ by more than about 20 seconds. The clotting time is influenced by various factors, particularly the time since the last meal and the nature of that meal. More than 4 or 5 hrs. after a meal, it is between 3 and 3.5 min.

A clinical method for the estimation of protein in urine and other body fluids. MARIAN C. SHEVYK AND D. D. STAFFORD. *Arch. Intern. Med.* 32, 222 (1923). Into a 15 cc. graduated centrifuge tube, pipet 8 cc. of urine, add 5 cc. Tsuchiya's reagent (1.5 g. phosphotungstic acid and 5 cc. concd. HCl dild. to 100 cc. with 95% EtOH) without mixing, stopper, invert slowly and exactly 1 min. later centrifuge for 15 min. at 1800 r. p. m. at 18–22°. Under these conditions, each 0.1 cc. pptd. protein is equiv. to 0.036 g. per 100 cc. If the vol. exceeds 1 cc. the detn. should be repeated with dild. urine. Comparison with detns. by heat coagulation and Kjeldahl show an av. error of 8.4% and a standard deviation of ±9.7%.

A new permanent standard for estimation of hemoglobin by the acid hematin method. E. E. OSGOOD AND H. D. HASKINS. *J. Biol. Chem.* 57, 107–10 (1923).—A soln. contg. 32 g. $\text{Fe}_2(\text{SO}_4)_3$ and 80 mg. $\text{Cr}_2(\text{SO}_4)_3$ in 100 cc. set at 15 min. nearly matches in color that of a 1% acid hematin soln. at 10 min. Different preps. of $\text{Fe}_2(\text{SO}_4)_3$ differ in color value and must be standardized. Temp. also affects the readings. A table is presented giving the concns. of acid hematin corresponding to readings from 8 to 16 mm. and at temps. from 15.5° to 25.5°. In order to develop the full color value of the acid hematin, immersion at 55–60° for 7 min. is recommended.

A new permanent standard for Sahli's hemoglobinometer. H. D. HASKINS. *J. Biol. Chem.* 57, 111–3 (1923); cf. preceding abstr. —A permanent standard for Sahli's hemoglobinometer is prepd. by mixing 30 cc. $\text{Fe}_2(\text{SO}_4)_3$ soln., contg. 53.3 g. per 100 cc., 15 cc. of soln. contg. 10 g. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 cc. and 10 cc. H_2O . The color comparison should be made at 19–20°.

A color test for water-soluble B. ALADÁR JENDRASSIK. *J. Biol. Chem.* 57, 129 (1923).—A no. of preps. obtained from various materials by different methods were used in a series of tests in an attempt to discover some chem. reaction for vitamin B. The only useful one appears to be the reduction of $\text{FeFe}(\text{CN})_6$. To the concd. H_2O soln. of the ext. add 2% of HIOAc and then a freshly prepd. mixt. of equal vols. of 0.1 N FeCl_3 and $\text{K}_3\text{Fe}(\text{CN})_6$. The tube is stoppered and set aside for 10 min. The color is observed and the liquid is dild. with from 1 to 5 vols. of H_2O . If a dark blue color or ppt. is not obtained, the test is negative. All exts. contg. vitamin B gave this reaction but it was consistently negative with exts. of vitamin-B-contg. foods made with solvents known not to extract B and was also negative with H_2O , HIOAc or dild. EtOH exts. of foods that did not contain B. After heating with alkalis, exts. originally contg. B no longer gave the reaction. Appropriate tests seemed to exclude phenols, amino acids and most alkaloids as substances responsible for this reaction.

A micro-colorimetric method of estimating the hydrogen-ion concentration in the blood. V. C. MYERS, H. W. SCHMITZ AND LELA E. BOONER. *J. Biol. Chem.* 57, 209–16 (1923).—A modification of Cullen's method (*C. A.* 16, 2700). The blood is drawn without stasis into a glass syringe contg. mineral oil and is then discharged into a Pyrex glass tube having a bulb at the lower end holding 1, 2 or 5 cc. The bulb contains a little $\text{K}_2\text{C}_2\text{O}_4$ and some mineral oil. The tip of the needle is introduced below the oil and the tube is filled to the constriction with blood and is then centrifuged. The 0.3% NaCl soln., contg. 10 cc. 0.002% phenol red per 100 cc., and adjusted to p_H 7.4–7.5, is kept in an inverted flask into which only CO_2 -free air may pass as the soln. is withdrawn. Under oil, 2 cc. are delivered into the cup of the bicolorimeter (*C. A.* 17, 781). A tuberculin syringe contg. a little oil is introduced into the bulb tube, some of the plasma is withdrawn and 0.1 cc. is discharged into the cup. The mixt. is stirred and the color comparison is made. The wedges of the colorimeter contain, resp., M/15 phosphate solns. of p_H 8.0 and 6.8, each contg. 0.1 vol. of 0.02% phenol red soln. The instrument is calibrated with 9 M/15 phosphate solns. covering range from p_H 7.0 to 7.8. If the plasma is cloudy, the third wedge contg. H_2O , a few drops milk and HCHO may be used.

Cullen's corrections for diln. and temp. are used. The 5 cc. bulb tube is needed only when CO_2 is also to be detd. Plasma for this purpose is withdrawn with an Ostwald pipet graduated between marks and fitted with stopcock and rubber bulb at the upper end.

I. GREENWALD

The determination of fibrinogen by precipitation with sodium sulfate compared with the precipitation of fibrin by the addition of calcium chloride. P. E. HOWE. *J. Biol. Chem.* 57, 235-40(1923).—The results obtained by various recalcification methods for the detn. of fibrin in oxalated plasma were compared with those obtained by the addn. of 10.6% Na_2SO_4 (0.75 *M*) and detn. of N in the filtrate and in untreated plasma. The results were identical within the limits of error. Instead of Na_2SO_4 , one may use 1 *M* Li_2SO_4 , 1.25 *M* MgSO_4 , 0.9 *M* mixt. of NaH_2PO_4 and Na_2HPO_4 (1:2), 1.125 *M* of a similar mixt. of KH_2PO_4 and K_2HPO_4 , or a 3.75 *M* soln. of NaCl . I. C.

The interconvertibility of creatine and creatinine. V. Estimation of creatine in muscle. AMANDUS HAHN AND L. SCHÄFER. *Z. Biol.* 78, 155-60(1923); cf. C. A. 17, 3547.

—The muscles are extd. with boiling 5% NaCl soln. contg. AcOH and then with boiling water. Any proteins in the combined exts. are pptd. with trichloroacetic acid, which avoids adsorption of creatine and creatinine, and the creatine is then detd. colorimetrically. Results are given for various muscles, which indicate that previous methods gave rather low results. J. C. S.

Cyanamide action. III. Quantitative cyanamide estimation in tissues. HANNS RAIDA. *Z. ges. expl. Med.* 31, 215-20(1923).—Cyanamide is isolated from aq. soln., blood and minced tissues by extn. with Et_2O and pptn. with ammoniacal Ag soln. Addn. of kieselsoln. aids filtration. The filtered ppt. is washed with NH_4OH soln. and dissolved in 5 cc. HNO_3 and titrated with 0.01 *N* NH_4CNS . 94-96% yields are obtained. The toxicity and metabolism of cyanamide in the body are not affected by giving alc. Hesse's finding that cyanamide is converted by the organism into urea and excreted is confirmed. E. R. LONG

Microchemical method for the determination of iron in one cc. of blood. G. FONTES AND L. THIVOLLE. *Compt. rend. soc. biol.* 88, 752-4(1923).—Measure accurately 0.3-1 cc. of blood and rinse the pipet twice with water. Add enough satd. aq. picric acid to bring the total vol. to 10 times the original blood amt. Filter and wash the ppt. on the paper; dry in an oven, transfer to a crucible and incinerate. Reduce the oxide by passing pure H over it (at dull red heat). Cool the crucible in a current of H . Dissolve the reduced Fe in a special phosphomolybdic reagent, made by boiling 40 g. $(\text{NH}_4)_2\text{MoO}_4$ and 10 g. NaOH in 100 cc. H_2O until the NH_3 is boiled off, adding 250 cc. of H_2PO_4 and 0.5 g. CuCO_3 , boiling for 15 min. and making the soln. up to 1 l. The blue color of the suboxide of Mo which develops when the Fe is changed to the FeO_3 state is now measured by titration with a 0.08% KMnO_4 until the color disappears. The KMnO_4 is standardized by means of ferrous ammonium sulfate 1.4 g. and 1 cc. concd. H_3PO_4 in a l. S. MORGULIS

Formulation of methods of experimentation in animal production. E. S. FORBES, H. S. GRINDLEY, F. B. MORRISON, C. H. ECKLES, C. R. MOULTON AND H. P. ARMSBY. *Bull. Nat. Research Council* 6, [2] 54 pp.(1923).—"Research work is conducted in the main by orderly methodical procedures, the underlying principles and many of the details of which may be definitely expressed, and must be clearly understood and faithfully followed, if the exptl. program is to lead to consistent and comparable results. Great improvement awaits the standardization and rationalization of methods—not as a means for the regulation of genius, but for the elimination of bad logic and inefficient procedure." The formulations of this paper are classified under: (1) General procedure in animal experimentation, including plan of work, statement of the problem, study of literature, choice and management of animals. (2) Detn. of digestion coeff. and N and mineral balances. (3) Detn. of total balance of matter and energy. (4) Feeding expts. (5) Bibliography. L. W. RIGGS

Small quantities of antimony and bismuth in biological liquids. CULLE AND E. VIEL. *Compt. rend.* 176, 1759-61(1923); cf. C. A. 17, 2289.—The object of this paper is to describe a simple and rapid procedure for detg. Sb and Bi in urine and other biological liquids and especially to enable clinicians to observe the elimination of these elements when used therapeutically. The principal reagent in this test consists of antipyrine 1 g., Kf 2, H_2O up to 30 cc. This gives a golden yellow ppt. with solns. of SbCl_3 , sensitive to 1 in 20000, or if the pptn. is made on a slide and observed with a microscope, 1 in 200000. With Hg the reagent gives a yellowish white and with Fe a rust-colored ppt. Liquids to be tested must not come in contact with Fe app., and blood must be absent. Ten cc. of cerebrospinal liquid or 100 cc. of urine are evapd. to dryness in a quartz capsule on the water bath, the residue is incinerated in a muffle aided by a few